

10/827,448

(FILE 'HOME' ENTERED AT 22:15:00 ON 10 DEC 2004)

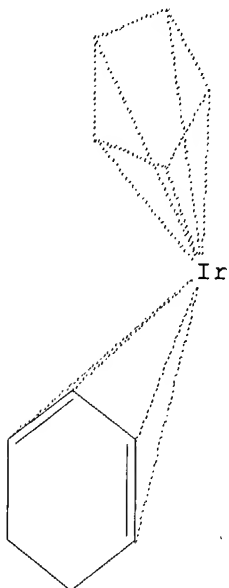
FILE 'REGISTRY' ENTERED AT 22:15:14 ON 10 DEC 2004

L1 STRUCTURE UPLOADED

=> d l1

L1 HAS NO ANSWERS

L1 STR



Structure attributes must be viewed using STN Express query preparation.

=> s l1

SAMPLE SEARCH INITIATED 22:15:47 FILE 'REGISTRY'

SAMPLE SCREEN SEARCH COMPLETED - 2541 TO ITERATE

39.4% PROCESSED 1000 ITERATIONS

9 ANSWERS

INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)

SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE \*\*COMPLETE\*\*

BATCH \*\*COMPLETE\*\*

PROJECTED ITERATIONS: 47797 TO 53843

PROJECTED ANSWERS: 171 TO 743

L2 9 SEA SSS SAM L1

=> s l1 full

FULL SEARCH INITIATED 22:15:52 FILE 'REGISTRY'

FULL SCREEN SEARCH COMPLETED - 51152 TO ITERATE

100.0% PROCESSED 51152 ITERATIONS

470 ANSWERS

SEARCH TIME: 00.00.01

L3 470 SEA SSS FUL L1

=> fil caplus

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

FULL ESTIMATED COST

ENTRY	SESSION
155.42	155.63

FILE 'CAPLUS' ENTERED AT 22:15:57 ON 10 DEC 2004  
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FILE COVERS 1907 - 10 Dec 2004 VOL 141 ISS 25  
FILE LAST UPDATED: 9 Dec 2004 (20041209/ED)

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> s 13

L4 71 L3

=>

=> s 14 and py<2003

22557546 PY<2003

L5 62 L4 AND PY<2003

=> d 1-62 bib abs

L5 ANSWER 1 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 2003:759354 CAPLUS

DN 139:247809

TI Gasohol composition for automobiles

IN Duan, Yurong; Li, Xianjun; Xu, Zhongkang; Zhang, Tingxun; Xue, Fangquan;  
Chen, Weiyuan; Shao, Yizhi

PA Peop. Rep. China

SO Faming Zhuanli Shenqing Gongkai Shuomingshu, 5 pp.  
CODEN: CNXXEV

DT Patent

LA Chinese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	CN 1381551	A	20021127	CN 2002-113610	20020415 <--
PRAI	CN 2002-113610		20020415		

AB The title composition comprises MeOH, gasoline, 0.005-0.01% of a solutizer and 0.001-0.005% of a combustion improver such as ferrocene. The ratio of MeOH to gasoline is 3:7-7:3, and the solutizer is preferably alkyl phosphates and/or C3-7 isoalkyl alc. The composition is superior in stability, high octane value and reducing noxious emissions.

L5 ANSWER 2 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 2002:881458 CAPLUS

DN 139:350763

TI Product class 6: organometallic complexes of iridium

AU O'Connor, J. M.  
CS Dept. of Chemistry & Biochemistry, University of California - San Diego,  
La Jolla, CA, 92093-0358, USA  
SO Science of Synthesis (2002), 1, 617-744  
CODEN: SSCYJ9  
PB Georg Thieme Verlag  
DT Journal; General Review  
LA English  
AB A review on the preparation and applications of iridium organometallic  
complexes.  
RE.CNT 373 THERE ARE 373 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 3 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 2002:659189 CAPLUS  
DN 138:39384  
TI Differentiation of planar chiral enantiomers of [Cp\*M(2-alkyl-  
phenoxo)][BF4] (M = Rh, Ir) by the trisphat anion  
AU Amouri, Hani; Thouvenot, Rene; Gruselle, Michel  
CS Laboratoire de chimie organique et matériaux moléculaires, UMR 7071 CNRS,  
université Pierre-et-Marie-Curie (Paris-6), Paris, 75252, Fr.  
SO Comptes Rendus Chimie (2002), 5(4), 257-262  
CODEN: CRCOCR; ISSN: 1631-0748  
PB Editions Scientifiques et Médicales Elsevier  
DT Journal  
LA English  
AB Precursor oxo-dienyl rhodium and iridium complexes [(η5-Cp\*)M(η5-2-  
alkyl-oxodienyl)][BF4] (2a-c) were prepared according to literature  
procedure. Addition of [n-Bu4N][Δ-trisphat] (6) to a CD2Cl2 solution of  
these chiral derivs. has led to the NMR differentiation of the  
enantiomers. These results pave the way towards the preparation of  
enantiomerically pure o-quinone methide complexes.  
RE.CNT 22 THERE ARE 22 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 4 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 2002:129857 CAPLUS  
DN 136:325678  
TI (η5-Pentamethylcyclopentadienyl)rhodium and -iridium Complexes with  
Weakly and Strongly Coordinating Anions: Isolation and First X-ray  
Molecular Structures of the Tris(solvent) Complexes  
[(C5Me5)M(acetone)2(H2O)][BF4]2 (M = Rh, Ir)  
AU Amouri, Hani; Guyard-Duhayon, Carine; Vaissermann, Jacqueline; Rager,  
Marie Noelle  
CS Laboratoire de Chimie Inorganique et Matériaux Moléculaires, UMR  
7071-CNRS, Université Pierre et Marie Curie, Paris, 75252, Fr.  
SO Inorganic Chemistry (2002), 41(6), 1397-1403  
CODEN: INOCAJ; ISSN: 0020-1669  
PB American Chemical Society  
DT Journal  
LA English  
OS CASREACT 136:325678  
AB Several novel pentamethylcyclopentadienyl complexes [(C5Me5)IrL3][BF4]2  
were prepared including the tris(solvent) precursors  
[(C5Me5)M(acetone)2(H2O)][BF4]2 (M = Rh, Ir) (1a,b). The x-ray mol.  
structures of 1a,b were determined at low temperature. Complexes 1a,b are  
isostructural, and both compds. crystallize in the monoclinic space group  
P21/c with a 10.157(3), b 14.038(9), c 16.335(2) Å, β  
99.73(2)°, and Z = 4 for 1a and with a 10.107(9), b 13.994(16), c  
15.996(34) Å, β 99.61(12)°, and Z = 4 for 1b. The  
coordinated H2O mol. is H bonded to both BF4- anions. Reaction of 1a,b  
with pyridine (py) afforded the related tris(pyridine) complexes

[(C5Me5)M( $\eta$ 1-(N)-py)3][BF4]2 (M = Rh, Ir) (2a,b). Also, the authors prepared the novel neutral compds. (C5Me5)M( $\eta$ 2-NO3)( $\eta$ 1-NO3) (M = Rh, Ir) (4a,b) where the anions are bonded to the metal center instead of a coordinating solvent as confirmed by x-ray study on the Ir complex 4b. The latter crystallizes in the orthorhombic space group Pcab with a 13.032(4), b 14.370(11), c 14.839(18) Å, and Z = 8.

RE.CNT 30 THERE ARE 30 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 5 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 2002:44863 CAPLUS  
DN 136:355318  
TI Syntheses and crystal structures of mononuclear [2.2]paracyclophane complexes of rhodium and iridium supported by the pentamethylcyclopentadienyl ligand [M( $\eta$ 6-pcp)( $\eta$ 5-C5Me5)](BF4)2 (M = Rh and Ir)  
AU Maekawa, Masahiko; Hashimoto, Naoki; Kuroda-Sowa, Takayoshi; Suenaga, Yusaku; Munakata, Megumu  
CS Research Institute for Science and Technology, Kinki University, Higashi-Osaka, 577-8502, Japan  
SO Inorganica Chimica Acta (2002), 328, 254-258  
CODEN: ICHAA3; ISSN: 0020-1693  
PB Elsevier Science S.A.  
DT Journal  
LA English  
OS CASREACT 136:355318  
AB Mononuclear [2.2]paracyclophane complexes of Rh and Ir, [M( $\eta$ 6-pcp)( $\eta$ 5-C5Me5)](BF4)2 (M = Rh (1) and Ir (2); pcp = [2.2]paracyclophane) were crystallized and their structures were 1st characterized crystallog. On both pcp complexes the metal atom is bonded to the benzene ring on one side of the pcp ligand in the  $\eta$ 6-coordination mode. The metal atom is also supported by the  $\eta$ 5-C5Me5 ligand to afford a triple-decker sandwich structure. In Rh pcp complex 1 the average Rh-C(pcp) and Rh-C(C5Me5) distances are 2.284(2) and 2.161(2) Å, resp. The average C(pcp):C(pcp) distance of 1.407(4) Å with the Rh atom is longer than that (1.388(4) Å) without a Rh atom. Similarly, the average Ir-C(pcp) and Ir-C(C5Me5) distances in Ir pcp complex 2 are 2.275(3) and 2.174(3) Å, resp. The average C(pcp):C(pcp) distance of 1.410(4) Å with the Ir atom is longer than that (1.388(4) Å) without an Ir atom. It is interesting that the average interannular distances of 2.97 Å for 1 and 2 between two decks of the pcp ligand are shorter than that (3.09 Å) of the metal-free pcp ligand, indicative of the decrease of the repulsive  $\pi$ -interaction between benzene rings. The Rh pcp complex gave the well-resolved 1H NMR signals of [Rh( $\eta$ 6-pcp)( $\eta$ 5-C5Me5)]2+, whereas the Ir pcp complex exhibited two kinds of 1H NMR signals which were assigned as [Ir( $\eta$ 6-pcp)( $\eta$ 5-C5Me5)]2+ and [Ir2( $\eta$ 6-pcp)( $\eta$ 5-C5Me5)2]4+ in (CD3)2CO at 23°.

RE.CNT 31 THERE ARE 31 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 6 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 2000:579167 CAPLUS  
DN 133:309997  
TI Steric control over arene coordination to  $\beta$ -diiminate rhodium(I) fragments  
AU Budzelaar, Peter H. M.; Moonen, Nicolle N. P.; De Gelder, Rene; Smits, Jan M. M.; Gal, Anton W.  
CS Department of Inorganic Chemistry, University of Nijmegen, Nijmegen, 6525 ED, Neth.  
SO Chemistry--A European Journal (2000), 6(15), 2740-2747  
CODEN: CEUJED; ISSN: 0947-6539  
PB Wiley-VCH Verlag GmbH

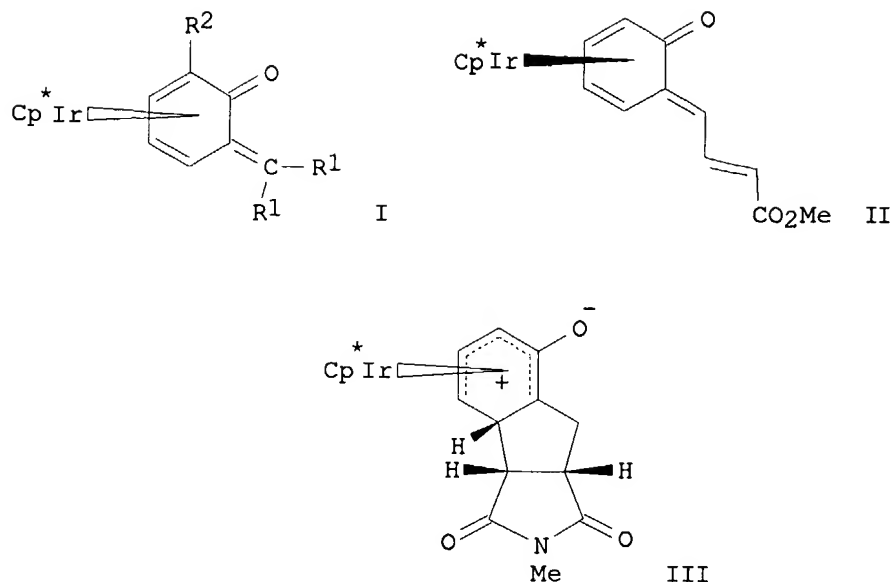
DT Journal  
LA English  
OS CASREACT 133:309997  
AB The bulky ligands Lx- (Lx = (2,6-X2C6H3)N:CMcCHCMe:N(C6H3X2-2,6), X = Cl, Me) can be used to generate fluxional mononuclear arene complexes [LxRh( $\eta^4$ -arene)] (arene = benzene, toluene, m-xylene, mesitylene), which for X = Me disproportionate to fluxional dinuclear complexes [[LMeRh]2(anti- $\mu$ -arene)]. For both mononuclear and dinuclear complexes, steric interactions do not stop the fluxionality but govern the preferred orientation of the Me-substituted arenes, thus allowing indirect determination of the static NMR parameters. For the  $\mu$ -arene complexes, two distinct types of fluxionality are proposed on the basis of calcs.: ring rotation and metal shift. In the solid state, the toluene complex has an  $\eta^4(1,2,3,4):\eta^4(3,4,5,6)$ -bridged structure; the NMR anal. indicates that the benzene and m-xylene complexes have similar structures. The mesitylene complex, however, has an unprecedented  $\eta^3(1,2,3):\eta^3(3,4,5)$ -bridged structure, which is proposed to correspond to the transition state for arene rotation in the other cases. Steric factors are thought to be responsible for this reversal of stabilities.

RE.CNT 27 THERE ARE 27 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 7 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 2000:277744 CAPLUS  
DN 133:74131  
TI A DFT investigation of the molecular and electronic structures of 19-electron transition-metal sandwich complexes  
AU Ogliaro, Francois; Halet, Jean-Francois; Astruc, Didier; Saillard, Jean-Yves  
CS Laboratoire de Chimie du Solide et Inorganique Moleculaire (CNRS UMR 6511), Universite de Rennes 1, Rennes, 35042, Fr.  
SO New Journal of Chemistry (2000), 24(5), 257-259  
CODEN: NJCHE5; ISSN: 1144-0546  
PB Royal Society of Chemistry  
DT Journal  
LA English  
AB DFT calcs. indicate that the 19-electron transition-metal complexes [Fe(C5R5)(C6R'6)] (R,R' = H,Me) have a metal-centered SOMO, a rather flexible mol. structure and that in their ground state the arene ring does not always adopt a perfect  $\eta^6$ -coordination mode.

RE.CNT 26 THERE ARE 26 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 8 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 2000:215361 CAPLUS  
DN 132:334605  
TI Stable o-Quinone Methide Complexes of Iridium: Synthesis, Structure, and Reversed Reactivity Imparted by Metal Complexation  
AU Amouri, Hani; Vaissermann, Jacqueline; Rager, Marie Noelle; Grotjahn, Douglas B.  
CS Laboratoire de Chimie Inorganique et Materiaux Moleculaires Unite CNRS 7071, Universite Pierre et Marie Curie, Paris, 75252, Fr.  
SO Organometallics (2000), 19(9), 1740-1748  
CODEN: ORGND7; ISSN: 0276-7333  
PB American Chemical Society  
DT Journal  
LA English  
OS CASREACT 132:334605  
GI



AB O-Quinone methides are important intermediates in biochem. and organic chemical, partly because of their high reactivity: the simplest compound o-quinone methide is unstable in condensed phases.  $\text{gtorsim.} -100^\circ$ . In contrast, here a general synthetic route to the 1st metal complex of o-quinone methide and complexes of several simple alkyl derivs. is reported. Coordination of 2-alkylphenols to  $[\text{Cp}^*\text{Ir}(\text{acetone})_3](\text{BF}_4)_2$  and subsequent deprotonation with  $\text{Et}_3\text{N}$  affords  $(\eta^5\text{-Cp}^*)\text{Ir}[\eta^5\text{-(2-alkyl)oxodienyl}](\text{BF}_4)$  complexes (5) in 85-90% yield. Deprotonation of 5 with KO-t-Bu gives 81-96% yields of neutral o-quinone methide complexes  $\text{Cp}^*\text{Ir}[\eta^4\text{-C}_6\text{H}_3\text{R}_1[:\text{C}(\text{R}_2)_2\text{O}]]$  [shown as I;  $\text{R}_1 = \text{R}_2 = \text{H}$  (6a);  $\text{R}_1 = \text{Me}$ ,  $\text{R}_2 = \text{H}$  (6b);  $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{Me}$  (6c);  $\text{R}_1 = \text{i-Pr}$ ,  $\text{R}_2 = \text{Me}$  (6d)], in which the  $\text{Cp}^*\text{Ir}$  fragment is coordinated in  $\eta^4$  fashion to the two C-C double bonds of the six-membered ring. The remarkable stability of the complexes allows characterization of their structure and reactivity. The x-ray mol. structure of 6d and 1-dimensional and 2-dimensional NMR studies on 6a and 6c are reported, showing the pronounced effects of  $\text{Cp}^*\text{Ir}$  coordination to the o-quinone methide ligand, particularly a strong upfield  $^{13}\text{C}$  chemical shift for the exocyclic C  $[:\text{C}(\text{R}_2)_2]$  of the uncoordinated C-C double bond. Although stable under Ar at room temperature,  $\text{Cp}^*\text{Ir}$ -o-quinone methide complexes 6 exhibited unusual reactivity toward acids or electrophiles; for instance treatment of 6a with 1 equiv of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  or I2 lead to the oxodienyl complexes  $[\text{Cp}^*\text{Ir}(\eta^5\text{-C}_7\text{H}_7\text{O})](\text{BF}_4)$  (5a) or  $[\text{Cp}^*\text{Ir}(\eta^5\text{-C}_7\text{H}_6\text{IO})](\text{I})$  (8), resp. Moreover, when complex 6a was treated with Me propynoate, a new o-quinone methide complex (shown as II) was obtained as a result of a coupling reaction between the electrophilic alkyne and the exocyclic C  $(:\text{CH}_2)$  of complex 6a. Finally, treatment of 6a with N-methylmaleimide gave the tricyclic Ir complex (shown as III) as a result of an unprecedented  $[2+3]$  cycloaddn. with part of the o-quinone methide complex 6a. The above reactions and  $^{13}\text{C}$  NMR evidence show that in o-quinone methide complexes 6 the exocyclic C  $[:\text{C}(\text{R}_2)_2]$  is nucleophilic, opposite of what is reported for free, electrophilic o-quinone methides. The difference in reactivity is attributed to the  $\text{Cp}^*\text{Ir}$  unit, which modifies dramatically the electronic properties of the o-quinone methide ligand.

RE.CNT 79      THERE ARE 79 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

AN 1999:129311 CAPLUS  
 DN 130:282156  
 TI Unusual Me-O Bond Cleavage in a Metalated Crown-Ether: X-ray Molecular Structure of (5-Methoxy-4,6-dimethyl-1,3-xylylene-2-one)-15 Crown-4 Complex of Pentamethylcyclopentadienyl Iridium  
 AU Amouri, H.; Vaissermann, J.; Rager, M. N.; Besace, Y.  
 CS Laboratoire de Chimie de Metaux de Transition, Universite Pierre et Marie Curie, Paris, F-75252, Fr.  
 SO Inorganic Chemistry (1999), 38(6), 1211-1215  
 CODEN: INOCAJ; ISSN: 0020-1669  
 PB American Chemical Society  
 DT Journal  
 LA English  
 AB The reaction of [(C5Me5)Ir(Solvent)3][BF4]2 (1) with (2,5-dimethoxy-4,6-dimethyl-1,3-xylylene)-15 crown-4 (2) affords the metalated crown-ether complex [(η5-C5Me5)Ir(η6-C18H28O6)][BF4]2 (3) in 88% yield. Complex 3 undergoes a facile Me-O bond cleavage to give the related semiquinone form of the metalated crown-ether [(η5-C5Me5)Ir(η5-C17H25O6)][BF4] (4). A single-crystal x-ray structure determination of complex 4 is reported. Complex 4 crystallizes in the monoclinic space group P21/m with a 8.187(5), b 17.193(4), and c 10.900(3) Å, α 90., β 109.68(1), γ 90., and Z = 2. The structure provides the authors with valuable information about the nature of the η5-semiquinone form of the metalated crown-ether and reveals that, surprisingly, the Me-O unit close to the crown chain is the one that undergoes hydrolysis. A rationale consistent with the exptl. results is advanced.

RE.CNT 20 THERE ARE 20 CITED REFERENCES AVAILABLE FOR THIS RECORD  
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 10 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1998:771699 CAPLUS  
 DN 130:110395  
 TI (η5-Pentamethylcyclopentadienyl)iridium(III) and -rhodium(III) labeling of amino acids with aromatic side-chains. The importance of relativistic effects for the stability of Cp\*IrIII sandwich complexes  
 AU Herebian, Diran Agaid; Schmidt, Claudia S.; Sheldrick, William S.; Van Wuelen, Christoph  
 CS Fakultät Chemie, Ruhr-Universität, Bochum, D-44780, Germany  
 SO European Journal of Inorganic Chemistry (1998), (12), 1991-1998  
 CODEN: EJICFO; ISSN: 1434-1948  
 PB Wiley-VCH Verlag GmbH  
 DT Journal  
 LA English  
 OS CASREACT 130:110395  
 AB (η5-Pentamethylcyclopentadienyl)iridium(III) and -rhodium(III) sandwich complexes [(η5-Cp\*)M(η6-aa)](CF3SO3)2 (M = Ir, Rh; aa = L-tyrosine, L-tryptophan, or L-phenylalanine derivs.) were prepared by treatment of [(η5-Cp\*)ML3](CF3SO3)2 (L = THF, Me2CO, MeCN) with the appropriate bio-ligand in THF for N-protected compds. and in CF3CO2H for α-amino acids with unprotected amino groups. Coordination to the Cp\*MIII fragments stabilizes the ketonic form of the tyrosine aromatic side-chains, leading to a marked enhancement in the acidity of the p-hydroxy function. The crystal structure of [Cp\*Ir(AcTyrOMe)](CF3SO3)2 (AcTyrOMe = N-acetyltyrosine Me ester) confirms a marked distortion towards an η5-oxohexadienyl coordination mode as may be gauged from the tilting of the 4-OH plane C(13)/C(14)/C(15) by no less than θ = 12.9° from that of the remaining ring atoms. Facial isomers are present in an effective 1:1 ratio for all tryptophan derivs. Whereas the Cp\*IrIII sandwich complexes of aromatic α-amino acids are stable in polar solvents, rapid decay is observed for analogous Cp\*RhIII complexes of

N-protected derivs. in polar solvents. Comparative nonrelativistic and relativistic all-electron d. functional calcns. on the cationic sandwich complexes  $[\text{Cp}^*\text{M}(\eta^6\text{-PhMe})]n^+$  ( $n = 2$ ,  $\text{M} = \text{Ir}$  or  $\text{Rh}$ ;  $n = 1$ ,  $\text{M} = \text{Ru}$ ) confirm that all 3 metals bind more tightly to  $\text{Cp}^*$  than to toluene as gauged by the resp. force consts. ( $k_1 > k_2$ ). A much larger relativistic enhancement of  $k_2$  for  $\text{M} = \text{Ir}$  (279 vs. 207  $\text{Nm}^{-1}$ ) could be responsible for the greater stability of  $\text{Cp}^*\text{IrIII}$  complexes in solution

RE.CNT 29 THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 11 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 1998:762337 CAPLUS  
DN 130:125199  
TI Ir-Mediated Nucleophilic Ortho-Functionalization of Phenols: Syntheses, Structures, Scope, and Limitation  
AU Amouri, Hani; Le Bras, Jean; Vaissermann, Jacqueline  
CS Ecole Nationale Supérieure de Chimie de Paris, URA CNRS 403, Paris, 75231, Fr.  
SO Organometallics (1998), 17(26), 5850-5857  
CODEN: ORGND7; ISSN: 0276-7333  
PB American Chemical Society  
DT Journal  
LA English  
OS CASREACT 130:125199  
AB Treatment of  $[\text{Cp}^*\text{Ir}(\eta^5\text{-PhO})][\text{BF}_4]$  (1) with hydride, deuteride, and C-, N-, and S-centered nucleophiles affords the stable  $\eta^4$ -phenol tautomers of the type  $[\text{Cp}^*\text{Ir}(\eta^4\text{-exo-2-(Nu)-C}_6\text{H}_5\text{O})]$  (2-6) {Nu = nucleophile}. In all cases regioselective nucleophilic addition occurs at the ortho-position relative to C:O with exo-stereochem. The x-ray mol. structure of the first neutral phenol tautomer  $[\text{Cp}^*\text{Ir}(\eta^4\text{-exo-2-(CH(OMe)}_2\text{)-C}_6\text{H}_5\text{O})]$  (4) was determined and provides valuable crystallog. information for an organic phenol tautomer. Oxidation of the novel dienone iridium complexes  $[\text{Cp}^*\text{Ir}(\eta^4\text{-exo-2-(Nu)-C}_6\text{H}_5\text{O})]$  by iodine provided a different type of products depending dramatically on the nature and electron properties of the 2-exo-nucleophile. For instance  $\text{R}_3\text{C-}$ ,  $\text{RO-}$ , and  $\text{R}_3\text{P-}$  centered nucleophiles gave the related ortho-functionalized phenols along with the starting material recycled in the form of  $[\text{Cp}^*\text{Ir}(\mu\text{-I})\text{I}]_2$ . In dramatic contrast N- and S-centered nucleophiles showed a retronucleophilic addition or C-Nu bond cleavage as demonstrated by complexes  $[\text{Cp}^*\text{Ir}(\eta^4\text{-2-exo-(N(CH}_2\text{)}_5\text{)-C}_6\text{H}_5\text{O})]$  and  $[\text{Cp}^*\text{Ir}(\eta^4\text{-2-exo-(SPh)-C}_6\text{H}_5\text{O})]$  to give the starting material identified spectroscopically and by x-ray structure as  $[\text{Cp}^*\text{Ir}(\eta^5\text{-PhO})][\text{I}]$ . In the latter, a rationale involving a one-electron oxidation process is proposed to explain the exptl. results.

RE.CNT 33 THERE ARE 33 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 12 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 1998:626709 CAPLUS  
DN 130:3940  
TI Activation and regioselective ortho-functionalization of phenols promoted by 'Cp\*Ir' fragment: synthesis, structures and applications to organic synthesis.  $\text{Cp}^* = \text{C}_5\text{Me}_5$   
AU Le Bras, Jean; Amouri, Hani; Vaissermann, Jacqueline  
CS URA CNRS 403, Ecole Nationale Supérieure de Chimie de Paris, Paris, 75231, Fr.  
SO Journal of Organometallic Chemistry (1998), 567(1-2), 57-63  
CODEN: JORCAI; ISSN: 0022-328X  
PB Elsevier Science S.A.  
DT Journal  
LA English  
OS CASREACT 130:3940



AB Several stable oxo-dienyl-Ir complexes  $[\text{Cp}^*\text{Ir}(\text{oxo-}\eta^5\text{-dienyl})][\text{BF}_4]$  were previously reported to be prepared in high to quant. yields. Treatment of these oxo-dienyl compds. with NaOMe afforded the corresponding novel neutral dienone complexes  $[\text{Cp}^*\text{Ir}(\text{oxo-}\eta^4\text{-dienone})]$ . Subsequent mild oxidation of the novel dienone-Ir complexes by  $\text{I}_2$  produced the related functionalized free phenols along with the starting organometallic material recycled in the form  $[\text{Cp}^*\text{Ir}(\mu\text{-I})\text{I}]_2$ . In this work the extension of this chemical to other type of nucleophiles such as phosphines, gave a stable Ir  $\eta^4$ -phenol tautomer complex  $[\text{Cp}^*\text{Ir}(\eta^4\text{-exo-2-(PMe}_3\text{)-C}_6\text{H}_5\text{O})][\text{BF}_4]$ . The latter was identified by x-ray diffraction and represents the key intermediate for the nucleophilic phenol functionalization reaction and the 1st mol. structure of a monocyclic phenol tautomer complex. Finally the use of the  $\text{Cp}^*\text{Ir}$  system in organic synthesis is presented and discussed.

RE.CNT 25 THERE ARE 25 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 13 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 1998:605668 CAPLUS  
DN 129:316360

TI Regioselective Phosphine Addition to  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^5\text{-oxocyclohexadienyl})]^+$  and X-ray Structure of the Stable Phenol Tautomer Complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^4\text{-exo-2-(PMe}_3\text{)C}_6\text{H}_5\text{O})]^+$ : A Key Intermediate for the Nucleophilic Phenol Functionalization Reaction

AU Le Bras, J.; Amouri, H.; Vaissermann, J.

CS Ecole Nationale Supérieure de Chimie de Paris, Paris, 75231, Fr.

SO Inorganic Chemistry (1998), 37(20), 5056-5060

CODEN: INOCAJ; ISSN: 0020-1669

PB American Chemical Society

DT Journal

LA English

OS CASREACT 129:316360

AB Treatment of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^5\text{-C}_6\text{H}_5\text{O})][\text{BF}_4]$  (1;  $\text{C}_6\text{H}_5\text{O} = 6\text{-oxo-2,4-cyclohexadien-1-yl}$ ) with an excess of trialkylphosphine ( $\text{PR}_3 = \text{PMe}_3$ ,  $\text{PEt}_3$ , and  $\text{PMe}_2\text{Ph}$ ) affords the  $\eta^4$ -phenol tautomers  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^4\text{-exo-2-(PR}_3\text{)C}_6\text{H}_5\text{O})][\text{BF}_4]$  (2-4) in which the phosphine nucleophile adds regioselectively at C-2. The x-ray mol. structure of such a phenol tautomer complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^4\text{-exo-2-(PMe}_3\text{)C}_6\text{H}_5\text{O})][\text{BF}_4]$  (2) is reported. Complex 2 crystallizes in the triclinic space group  $P_{\bar{1}}$  with  $a$  8.599(1),  $b$  9.0173(9),  $c$  14.448(3) Å,  $\alpha$  95.90(1),  $\beta$  99.47(1),  $\gamma$  99.20(1)°, and  $Z = 2$ . Oxidation of these  $\eta^4$ -dienone complexes 2-4 by  $\text{I}_2$  affords the related phosphine salts  $[(\text{C}_6\text{H}_4\text{OH)PR}_3][\text{BF}_4]$  (5-7), and the starting Ir complex is recycled as  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\mu\text{-I})\text{I}]_2 \cdot \text{I}_2$  (8) as confirmed by an x-ray anal. carried out on compds. 5 and 8. Complex 5 crystallizes in the monoclinic space group  $P2_1/c$  with  $a$  10.593(6),  $b$  19.922(4),  $c$  11.909(3) Å,  $\beta$  106.83(4)°, and  $Z = 8$ . The structure of 8 can be viewed as an infinite chain of dimeric Ir  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\mu\text{-I})\text{I}]_2$  bridged by  $\text{I}_2$  units. Complex 8 crystallizes in the monoclinic space group  $P2_1/c$  with  $a$  15.533(3),  $b$  8.374(1),  $c$  23.541(4) Å,  $\beta$  100.89(4)°, and  $Z = 4$ .

RE.CNT 30 THERE ARE 30 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 14 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 1998:373221 CAPLUS  
DN 129:122744

TI General Synthesis, First Crystal Structure, and Reactivity of Stable o-Quinone Methide Complexes of  $\text{Cp}^*\text{Ir}$

AU Amouri, Hani; Besace, Yvon; Le Bras, Jean; Vaissermann, Jacqueline

CS Ecole Nationale Supérieure de Chimie de Paris, Paris, 75231, Fr.

SO Journal of the American Chemical Society (1998), 120(24),

6171-6172

CODEN: JACSAT; ISSN: 0002-7863

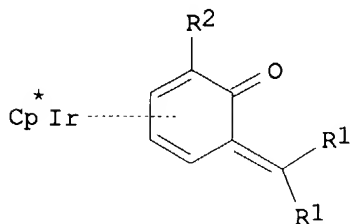
PB American Chemical Society

DT Journal

LA English

OS CASREACT 129:122744

GI



I

AB A general and unprecedented synthetic procedure to isolate and fully characterize a series of  $\eta^4$ -o-quinone methide complexes I (Cp\* = pentamethylcyclopentadienyl; R1 = H, R2 = H, Me; R1 = Me, R2 = H, i-Pr) including the simplest o-quinone methide, obtained as an iridium complex I (R1 = R2 = H) is described. Thus, reaction of oxo-dienyl iridium complexes [Cp\*Ir(oxo- $\eta^5$ -dienyl)][BF4] with t-BuOK in CH2Cl2 gave I. The mol. structure of I (R1 = Me, R2 = i-Pr) was unambiguously identified by X-ray crystallog.

RE.CNT 28 THERE ARE 28 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 15 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1998:244764 CAPLUS

DN 129:16221

TI  $\eta^4$ -Quinone,  $\eta^5$ -semiquinone and  $\eta^6$ -hydroquinone complexes of pentamethylcyclopentadienyl iridium. X-ray molecular structure of [Cp\*Ir( $\eta^4$ -1,4 benzoquinone)]

AU Le Bras, Jean; Amouri, H.; Vaissermann, Jacqueline

CS URA, CNRS 403, Ecole Nationale Supérieure de Chimie de Paris, Paris, 75231, Fr.

SO Journal of Organometallic Chemistry (1998), 553(1-2), 483-485

CODEN: JORCAI; ISSN: 0022-328X

PB Elsevier Science S.A.

DT Journal

LA English

OS CASREACT 129:16221

AB Treatment of hydroquinone with [Cp\*Ir(solvent)3][BF4]2 (1) in acidic medium afforded the stable  $\pi$ -bonded complex [Cp\*Ir( $\eta^6$ -hydroquinone)][BF4]2 (2) in high yield. Complex 2 can be easily deprotonated by a base to give the related [Cp\*Ir( $\eta^5$ -semiquinone)][BF4] (3) and [Cp\*Ir( $\eta^4$ -quinone)] (4) compds. identified by spectroscopic methods. Complex 4 reacts with an excess of HBF4·Et2O to give the starting material 2 quant. These chemical transformations occur with facile reversible changes of the oxidation state from Ir(III) to Ir(I). Further the x-ray mol. structure of 4 is reported.

RE.CNT 13 THERE ARE 13 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 16 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1998:127065 CAPLUS

DN 128:167550  
 TI p-, o- $\eta$ 4-Benzoquinone and the Related  $\eta$ 6-Hydroquinone,  
 $\eta$ 6-Catechol Complexes of Pentamethylcyclopentadienyliridium:  
 Synthesis, Structures and Reactivity  
 AU Le Bras, Jean; Amouri, H.; Vaissermann, Jacqueline  
 CS Ecole Nationale Supérieure de Chimie de Paris, Paris, 75231, Fr.  
 SO Organometallics (1998), 17(6), 1116-1121  
 CODEN: ORGND7; ISSN: 0276-7333  
 PB American Chemical Society  
 DT Journal  
 LA English  
 OS CASREACT 128:167550  
 AB Treatment of hydroquinone with  $[\text{Cp}^*\text{Ir}(\text{solvent})_3][\text{BF}_4]_2$  in acidic medium  
 afforded the stable  $\pi$ -bonded complex  $[\text{Cp}^*\text{Ir}(\eta^6\text{-hydroquinone})][\text{BF}_4]_2$   
 (2) in 93% yield. Complex 2 can be easily deprotonated by a base to give  
 the related  $[\text{Cp}^*\text{Ir}(\eta^5\text{-semiquinone})][\text{BF}_4]$  (3) and  $[\text{Cp}^*\text{Ir}(\eta^4\text{-p-}$   
 $\text{benzoquinone})]$  (4) compds., identified by spectroscopic methods. Further,  
 the x-ray mol. structure of p-benzoquinone iridium complex 4 is reported;  
 such compds. are rare in the literature. Complex 4 reacts with an excess  
 of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  to give the starting material 2 quant. Interestingly,  
 the chemical transformations from 2 to 4 and vice versa occur with facile  
 reversible changes of the oxidation state from Ir(III) to Ir(I). On the  
 other hand, the oxo-dienyl iridium complex  $[\text{Cp}^*\text{Ir}(\eta^5\text{-2,6-dimethoxy-}$   
 $\text{C}_6\text{H}_3\text{O})][\text{BF}_4]$  (5), identified by spectroscopic methods and x-ray anal.,  
 reacts with NaOMe in methanol to give unexpectedly but reproducibly the  
 substituted o-benzoquinone iridium compound  $[\text{Cp}^*\text{Ir}(\eta^4\text{-(3-methoxy)-o-}$   
 $\text{benzoquinone})]$  (6). The solution behavior and the reactivity of 6, as well  
 as a rationale explaining its formation, is advanced.  
 RE.CNT 27 THERE ARE 27 CITED REFERENCES AVAILABLE FOR THIS RECORD  
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 17 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1997:782980 CAPLUS  
 DN 128:140839  
 TI Unexpected formation of  $\text{Cp}^*\text{IrCl}_2\text{PPh}_3$  from the reaction of  
 $[\text{Cp}^*\text{Ir}(\eta^5\text{-C}_6\text{H}_5\text{O})][\text{BF}_4]$  with PPh<sub>3</sub> in dichloroethane involving C-Cl bond  
 activation  
 AU Le Bras, J.; Amouri, H.; Vaissermann, J.  
 CS rue Pierre et Marie Curie, 11, Ecole Nationale Supérieure de Chimie de  
 Paris, 75231 Paris Cedex 05, URA CNRS 403, Fr.  
 SO Journal of Organometallic Chemistry (1997), 548(2), 305-307  
 CODEN: JORCAI; ISSN: 0022-328X  
 PB Elsevier Science S.A.  
 DT Journal  
 LA English  
 AB The reaction of  $[\text{Cp}^*\text{Ir}(\eta^5\text{-C}_6\text{H}_5\text{O})][\text{BF}_4]$  (1) with PPh<sub>3</sub> in refluxing  
 $\text{C}_2\text{H}_4\text{Cl}_2$  afforded unexpectedly but reproducibly the known compound  
 $\text{Cp}^*\text{IrCl}_2\text{PPh}_3$  (2) which was identified by <sup>1</sup>H NMR spectroscopy and single  
 crystal x-ray diffraction. This unexpected chemical transformation to give 2  
 involves 'C-Cl' abstraction from dichloroethane mediated by the 'Cp\*Ir'  
 fragment. A rationale for this surprising transformation is advanced.  
 RE.CNT 13 THERE ARE 13 CITED REFERENCES AVAILABLE FOR THIS RECORD  
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 18 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1997:690753 CAPLUS  
 DN 127:346518  
 TI  $\pi$ -Olefin-iridium Complexes. XXIV. Photoreactions of  $[\text{CpM}(\text{C}_2\text{H}_4)_2]$  (M =  
 Rh, Ir) with alkynes as a basis for novel  $\pi$ -complexes  
 AU Muller, Jorn; Akhnoukh, Talaat; Gaede, Petra Escarpa; Guo, Ao-ling; Moran,  
 Paul; Qiao, Ke  
 CS Inst. Anorganische Analytische Chemie Technischen Univ. Berlin, Berlin,

D-10623, Germany  
SO Journal of Organometallic Chemistry (1997), 541(1-2), 207-217  
CODEN: JORCAI; ISSN: 0022-328X  
PB Elsevier  
DT Journal  
LA German  
OS CASREACT 127:346518  
AB UV irradiation of [CpRh(C2H4)2] in pentane in the presence of alkynes C2R2 [R = Me (a); Et (b)] gives a variety of products, and several compds. have been isolated by chromatog. The  $\eta^4$ -benzene complexes [CpRhC6R6] (2a,b) and the rhodacyclopentadienyl species [Cp2Rh2C4R4] (3a,b) were obtained as main products. The isolable but highly reactive complexes [CpRh(C2H4)(C2R2)] (1a) act as precursors for 3 and for hexaalkylbenzene, and by hydrolysis during chromatog. also give the 1-rhoda-2-oxa-cyclohexa-3,5-diene compds. [Cp2Rh2C4R4O] (6a,b). Further isolated products are the bis( $\mu$ -vinyl) compound [Cp2Rh2(C2H3)(C2H3)(C2HMe2)] (4a) as well as the  $\eta^4$ -butadiene species [CpRh{C4HR4-C5H4Rh(C2H4)2}] (5a) the formation of which involves the unusual C-H activation of a Cp moiety. From the reaction mixture formed by UV irradiation of [CpIr(C2H4)2] in hexane only the  $\mu$ -vinyl species [Cp2Ir2(C2H3)2] (7) was isolated, while irradiation in the presence of butyne-2 yielded the  $\eta^4$ -hexamethylbenzene complex [CpIrC6Me6] (8). The Compds. 2b, 3b, 5a, and 8 were characterized by x-ray crystal anal.

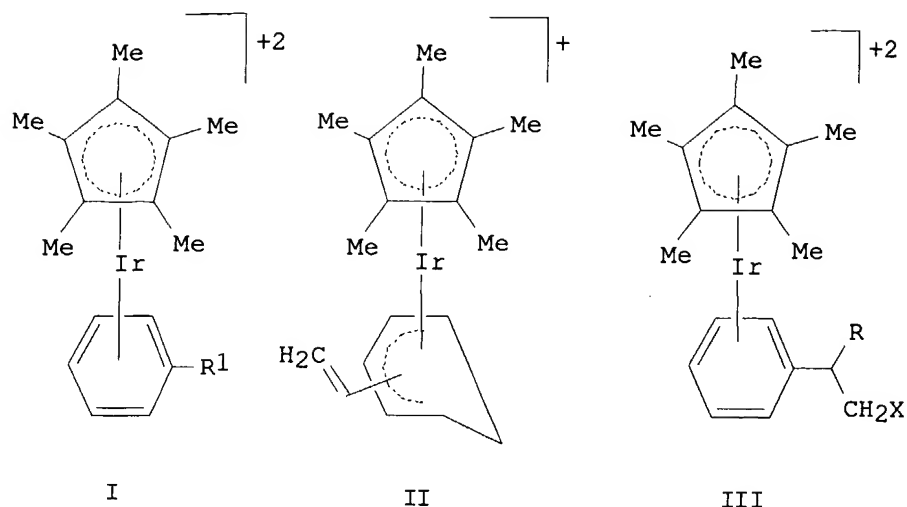
RE.CNT 30 THERE ARE 30 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 19 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 1997:436160 CAPLUS  
DN 127:149235  
TI Anion Binding within the Cavity of  $\pi$ -Metalated Calixarenes  
AU Staffilani, Mara; Hancock, Kirsty S. B.; Steed, Jonathan W.; Holman, K. Travis; Atwood, Jerry L.; Juneja, Ravindra K.; Burkhalter, Robert S.  
CS Departments of Chemistry, King's College London, London, WC2R 2LS, UK  
SO Journal of the American Chemical Society (1997), 119(27), 6324-6335  
CODEN: JACSAT; ISSN: 0002-7863  
PB American Chemical Society  
DT Journal  
LA English  
AB The synthesis of a range of bi- and tetrametalated macrocyclic complexes based upon calix[4]arenes p-tert-butylcalix[4]arene and related tetraalkoxy derivs., [(M(L))2(calixarene-nH)]X4-n and [(M(L))4(calixarene-2H)]X6 (M = Rh, Ir, Ru; L = Cp\*, p-MeC6H4CHMe2; n = 0, 1, 2; X = BF4, CF3SO3, HSO4, I, ReO4, H2PO4, etc., not all combinations) is reported. A related trimetallic calix[5]arene derivative [(Ir( $\eta^5$ -C5Me5))3(p-tert-butylcalix[5]arene-H)][BF4]5 also was synthesized. In all cases, the presence of the transition metal centers results in a significant enhancement in the acidity of the hydroxyl functionalities at the calixarene lower rim. For the tri- and tetrametalated derivs., the host-guest behavior of the calixarene is drastically altered such that anionic guest species are included within the mol. cavity. The function of the new tetrametallic hosts [(Ru( $\eta^6$ -p-MeC6H4CHMe2))4( $\eta^6$ : $\eta^6$ : $\eta^6$ : $\eta^6$ -C28H22O4)]6+ (15) and [(Ir( $\eta^5$ -C5Me5))4( $\eta^6$ : $\eta^6$ : $\eta^6$ : $\eta^6$ -C28H22O4)]6+ (16) as anion receptors was confirmed by x-ray crystal structure studies upon BF4- (15a, 16a), HSO4- (16c), SO42- (15c), and I- (15d) derivs., which clearly demonstrate a cooperative effect arising from the arrangement of four metal centers about a common, rigid binding pocket, resulting in anion-host contacts  $\geq 2.85$  Å (BF4...Ccalix). The anion binding properties of host 15 in aqueous solution also were studied by 1H NMR titration, giving binding consts. in the range 100-250 M-1 for nitrate and halide

anions, with the binding constant decreasing in the order  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ . Significantly increased binding is observed in nonaq. media. This novel form of anion complexation contrasts to the formation of weakly bound, van der Waals inclusion complexes commonly observed in calixarene chemical

L5 ANSWER 20 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 1997:383113 CAPLUS  
DN 127:65918  
TI Reduction of iridocenium salts  $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-L})]^+$  ( $\text{L} = \text{C}_5\text{H}_5$ ,  
C<sub>5</sub>Me<sub>5</sub>, C<sub>9</sub>H<sub>7</sub>); ligand-to-ligand dimerization induced by electron transfer  
AU Gusev, Oleg V.; Peterleitner, Mikhail G.; Ievlev, Mikhail A.; Kal'sin,  
Alexander M.; Petrovskii, Pavel V.; Denisovich, Larisa I.; Ustynyuk,  
Nikolai A.  
CS A.N. Nesmeyanov Institute of Organoelement Compounds, Academy of Sciences  
of Russia, Vavilov St. 28, 117813, Moscow, Russia  
SO Journal of Organometallic Chemistry (1997), 531(1-2), 95-100  
CODEN: JORCAI; ISSN: 0022-328X  
PB Elsevier  
DT Journal  
LA English  
AB Redox properties of Ir complexes  $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-L})]^+$  ( $1^+$ ,  $\text{L} =$   
C<sub>5</sub>H<sub>5</sub>;  $2^+$ ,  $\text{L} = \text{C}_5\text{Me}_5$ ;  $3^+$ ,  $\text{L} = \text{C}_9\text{H}_7$ ) were studied by cyclic voltammetry  
(CV). All three complexes can be reduced to 19-electron radicals 1-3.  
The stability and reactivity of these radicals depend on the electronic  
and steric properties of the ligands. The mixture of dimers  
 $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\mu\text{-}\eta^4\text{:}\eta^4\text{-C}_5\text{H}_5\text{C}_5\text{Me}_5)\text{Ir}(\eta^5\text{-C}_5\text{H}_5)]$  (4a) and  
 $[(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(\mu\text{-}\eta^4\text{:}\eta^4\text{-C}_5\text{Me}_5\text{C}_5\text{Me}_5)\text{Ir}(\eta^5\text{-C}_5\text{H}_5)]$  (4b) was  
formed as a result of reduction of  $1^+$  with Na/Hg in THF. Both chemical and  
electrochem. reduction of  $2^+$  gave the dimer  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\mu\text{-}$   
 $\eta^4\text{:}\eta^4\text{-C}_5\text{Me}_5\text{C}_5\text{Me}_5)\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)]$  (5) in low yield. Reduction of  $3^+$   
gave tetranuclear  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\mu\text{-}\eta^4\text{:}\eta^5\text{-C}_9\text{H}_7)\text{Ir}(\mu\text{-}$   
 $\eta^4\text{:}\eta^4\text{-C}_5\text{Me}_5\text{C}_5\text{Me}_5)\text{Ir}(\mu\text{-}\eta^5\text{:}\eta^4\text{-C}_9\text{H}_7)\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)]$  (6).  
RE.CNT 21 THERE ARE 21 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 21 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 1997:365302 CAPLUS  
DN 127:81577  
TI Iridium(III) complexes of  $\eta^6$ -arenes with olefinic and cyclopropyl  
substituents: facile conversion to  $\eta^3$ -phenylallyl complexes  
AU Jeong, Hyunmok; Joo, Kwang-Suk; Chin, Chong Shik  
CS Department of Chemistry, Sogang University, Seoul, 121-742, S. Korea  
SO Bulletin of the Korean Chemical Society (1997), 18(4), 402-405  
CODEN: BKCSDE; ISSN: 0253-2964  
PB Korean Chemical Society  
DT Journal  
LA English  
GI



AB Olefinic- and cyclopropyl-substituted arenes ( $C_6H_5R_1$ ) react with  $[Cp^*Ir(CH_3COCH_3)_3]Y_2$  ( $Y = ClO_4^-$ ,  $OTf^-$ ) (formed in situ) to give  $\eta^6$ -arene complexes  $I \cdot 2Y$  [ $R_1 = CH:CH_2$  (1a),  $CH:CHCH_3$  (1b),  $CMe:CH_2$  (1c), cyclopropyl (1d),  $Y =$  same as above]. Complex 1b-1d ( $Y = OTf^-$ ) are readily converted into  $\eta^3$ -allyl complexes,  $[Cp^*(MeCN)Ir(\eta^3-CHPhCHCH_2)]^+$  (2a) and  $[Cp^*(MeCN)Ir(\eta^3-CH_2CPhCH_2)]^+$  (2b), in the presence of  $Na_2CO_3$  in MeCN. The  $\eta^6$ -styrene complex, 1a ( $Y = ClO_4^-$ ), reacts with  $NaBH_4$  to give  $\eta^5$ -cyclohexadienyl complexes II (3 isomers: ortho/meta/para = 46/37/17), while with  $H_2$  it gives  $\eta^6$ -ethylbenzene complex III ( $R = X = H$ ). Complex 1a and 1c ( $Y = ClO_4^-$ ) react with  $HCl$  to give III ( $X = Cl$ ,  $R = H$ ,  $Me$ , resp.).

RE.CNT 12 THERE ARE 12 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 22 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1997:259377 CAPLUS

DN 126:349869

TI Anion inclusion within the cavity of  $\pi$ -metalated p-t-butylcalix[5]arene  
AU Steed, Jonathan W.; Johnson, Carl P.; Juneja, Ravindra K.; Atwood, Jerry L.; Burkhalter, Robert S.

CS Department Chemistry, University Missouri, Columbia, MO, 65211, USA

SO Supramolecular Chemistry (1996), 6(3-4), 235-238

CODEN: SCHEER; ISSN: 1061-0278

PB Gordon & Breach

DT Journal

LA English

AB The x-ray crystal structure of the triiridium p-t-butylcalix[5]arene host mol.  $[ \{ Ir(\eta^5-C_5Me_5) \}_3(p\text{-tert-butylcalix[5]arene-H}) ][BF_4]_5$  reveals the deep inclusion of one of the  $BF_4$  anions within the bowl-shaped cavity of the macrocycle. The compound is monoclinic, space group  $C2/c$ , with  $a$  46.388(8),  $b$  15.532(6),  $c$  31.816(6) Å, and  $\beta$  118.380(7)°;  $Z = 8$ .

L5 ANSWER 23 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1997:207695 CAPLUS

DN 126:251282

TI Activation and Regioselective Ortho-Functionalization of the A-Ring of  $\beta$ -Estradiol Promoted by "CpIr": An Efficient Organometallic Procedure for the Synthesis of 2-Methoxyestradiol

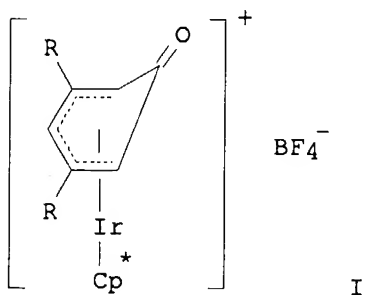
AU Le Bras, J.; Rager, M. N.; Besace, Y.; Amouri, H.; Vaissermann, J.

CS Ecole Nationale Supérieure de Chimie de Paris, URA CNRS 403, Paris, 75231,

Fr.  
 SO Organometallics (1997), 16(8), 1765-1771  
 CODEN: ORGND7; ISSN: 0276-7333  
 PB American Chemical Society  
 DT Journal  
 LA English  
 AB 5,6,7,8-Tetrahydro-2-naphthol and  $\beta$ -estradiol gave  $\eta^6$ -arene complexes using  $[\text{Cp}^*\text{Ir}(\text{solvent})_3][\text{BF}_4]_2$  prepared in situ; subsequent O-deprotonation with  $\text{NEt}_3$  produced the corresponding complexes  $[\text{Cp}^*\text{Ir}(\text{oxo-}\eta^5\text{-dienyl})][\text{BF}_4]$  (I). In the case of the complexed hormone, the  $\text{Cp}^*\text{Ir}$  moiety coordinates the A-ring either  $\alpha$  (metal down) or  $\beta$  (metal up) relative to the Me group at C(13). The X-ray mol. structure of the  $\alpha$ -isomer was determined. I react with  $\text{NaOMe}$  in methanol at  $-40^\circ\text{C}$  to give the novel iridium cyclohexadienone complexes  $[\text{Cp}^*\text{Ir}(\text{methoxy-}\eta^4\text{-dienone})]$  in 95 and 91% yields, resp., with nucleophilic attack occurring exclusively at the ortho-position relative to the C:O function. The novel iridium cyclohexadienone compound of the complexed steroid can be oxidized easily by iodine to produce 2-methoxyestradiol in 60% overall yield from  $\beta$ -estradiol. This efficient organometallic procedure is preferable to the classical organic procedure, which requires five steps and affords 2 in less than 5% yield. 2-Methoxyestradiol is an anticancer agent which possesses important antitumor effects in vivo.

RE.CNT 26 THERE ARE 26 CITED REFERENCES AVAILABLE FOR THIS RECORD  
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 24 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1996:721743 CAPLUS  
 DN 126:60105  
 TI Regioselective Ortho-Functionalization of Phenols Promoted by the " $\text{Cp}^*\text{Ir}$ ". Unit in  $[\text{Cp}^*\text{Ir}(\text{oxo-}\eta^5\text{-cyclohexadienyl})][\text{BF}_4]$  Complexes  
 AU Le Bras, Jean; El Amouri, Hani; Vaissermann, Jacqueline  
 CS Ecole Nationale Supérieure de Chimie de Paris, Paris, 75231, Fr.  
 SO Organometallics (1996), 15(26), 5706-5712  
 CODEN: ORGND7; ISSN: 0276-7333  
 PB American Chemical Society  
 DT Journal  
 LA English  
 OS CASREACT 126:60105  
 GI

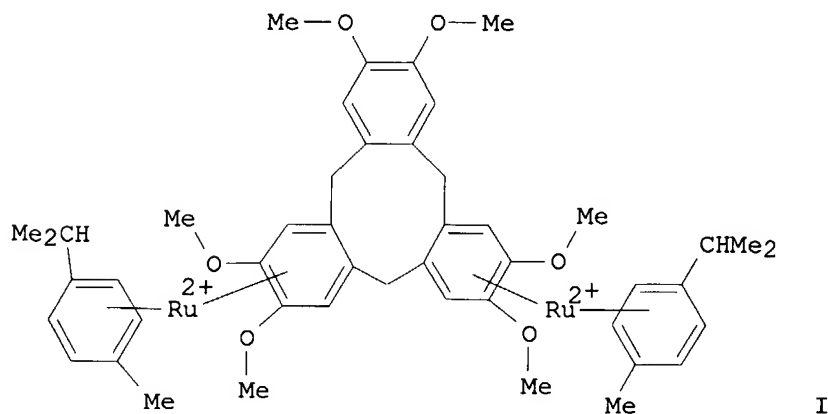


AB Alkylated phenols (phenol, 3,5-dimethylphenol and 3,4-dimethylphenol) were complexed by the  $[\text{Cp}^*\text{Ir}(\text{solvent})_3][\text{BF}_4]_2$  (1) unit prepared in situ; subsequent treatment with  $\text{NEt}_3$  produced the (oxo- $\eta^5$ -cyclohexadienyl)iridium complexes  $[\text{Cp}^*\text{Ir}(\eta^5\text{-C}_6\text{H}_3\text{R}_2\text{O})][\text{BF}_4]$  [R = H (2); R = Me (3, 4)]. The x-ray mol. structure of 3 (shown as I; R = Me) was determined. These (oxo- $\eta^5$ -cyclohexadienyl)iridium derivs. react with  $\text{NaOMe}$  in  $\text{MeOH}$  to give the novel Ir cyclohexadienone complexes

[Cp\*Ir( $\eta^4$ -C<sub>6</sub>H<sub>3</sub>R<sub>2</sub>O(OMe))] [R = H (5); R = Me (6, 7)] in 75-90% yield with nucleophilic attack occurring exclusively at the ortho-position relative to the C:O function. Addition of HBF<sub>4</sub>·Me<sub>2</sub>O to these Ir cyclohexadienone complexes 5-7 affords the starting material (oxo- $\eta^5$ -cyclohexadienyl)iridium derivs. 2-4 with MeOH. Further exposure to HBF<sub>4</sub>·Me<sub>2</sub>O produces the corresponding phenolic compds. [Cp\*Ir( $\eta^6$ -C<sub>6</sub>H<sub>3</sub>R<sub>2</sub>OH)](BF<sub>4</sub>)<sub>2</sub> (8-10); these chemical reactions are accompanied with hapticity changes  $\eta^4 \rightarrow \eta^5 \rightarrow \eta^6$  of the coordinated  $\pi$ -hydrocarbon. The novel Ir cyclohexadienone complexes 5-7 can be oxidized easily by I<sub>2</sub> to produce the free cyclohexadienones which rearomatize to give the free ortho-substituted phenols 11-13 in yields from 80% to quant.

RE.CNT 28 THERE ARE 28 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 25 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 1996:569666 CAPLUS  
DN 125:248084  
TI Inclusion of Neutral and Anionic Guests within the Cavity of  
 $\pi$ -Metalated Cyclotrivenatrylenes  
AU Holman, K. Travis; Halian, Martha M.; Jurisson, Silvia S.; Atwood, Jerry L.; Burkhalter, Robert S.; Mitchell, Andrew R.; Steed, Jonathan W.  
CS Departments of Chemistry, University of Missouri, Columbia, MO, 65211, USA  
SO Journal of the American Chemical Society (1996), 118(40), 9567-9576  
CODEN: JACSAT; ISSN: 0002-7863  
PB American Chemical Society  
DT Journal  
LA English  
GI



AB Treatment of the chloride bridged species  $[M(L)Cl(\mu-Cl)]_2$  (M = Ru, L = 4-MeC<sub>6</sub>H<sub>4</sub>CHMe<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, or C<sub>6</sub>Me<sub>6</sub>; M = Ir, L = C<sub>5</sub>Me<sub>5</sub>) with Ag salts AgX (X = BF<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>, CF<sub>3</sub>CO<sub>2</sub> etc.) followed by reflux with the bowl-shaped macrocycle cyclotrivenatrylene (CTV) results in the clean formation of mono-, di-, and trimetallic CTV complexes  $[M(L)]_n(CTV)X_{2n}$  (n = 1, 2, 3). Further salts (X = ReO<sub>4</sub><sup>-</sup>, I<sup>-</sup>) may be generated by anion metathesis. All three types of complex display novel host-guest properties. In the case of the monometallic hosts the disruption of the characteristic columnar packing mode of the CTV, a result of the presence of the metal center, leads to the inclusion of neutral and anionic guest species (NO<sub>2</sub>Me, Et<sub>2</sub>O, H(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub><sup>-</sup>, etc.) within the CTV cavity. For complexes where n = 2 or 3



the inclusion of anionic guests is invariably observed. The extent of anion binding was established by x-ray crystal structure detns. upon various di- and trimetallic species containing  $\text{BF}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ , or  $\text{ReO}_4^-$ , by radiotracer anal. in solution using  $^{99m}\text{TcO}_4^-$  and  $^{188}\text{ReO}_4^-$ , and by cyclic voltammetry. The trimetallic complex  $[\{\text{Ir}(\text{Cp}^*)\}_3(\text{CTV})][\text{BF}_4]_6$  (9a) in particular exhibits F...CCTV contacts as short as 2.78(3) Å. The dimetallic host  $[\{\text{Ru}(\eta^6\text{-4-MeC}_6\text{H}_4\text{CHMe}_2)\}_2(\eta^6\text{:}\eta^6\text{-CTV})]^{4+}$ , I, has a specific affinity for large tetrahedral anions and will selectively extract both  $^{99}\text{TcO}_4^-$  and  $\text{ReO}_4^-$  from aqueous solution, even in the presence of a large excess of  $\text{Cl}^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and to some extent  $\text{ClO}_4^-$ .

L5 ANSWER 26 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1995:1006067 CAPLUS

DN 124:176491

TI A study of  $\pi$ -complexation of phenol and  $\beta$ -estradiol by 'Cp\*M' M = Rh, Ir moieties: syntheses, solution behavior and reactivity; x-ray molecular structure of  $[\text{Cp}^*\text{Rh}(\eta^5\text{-C}_6\text{H}_5\text{O}\cdot\text{H}_2\text{O})][\text{BF}_4]$ ,  $\text{Cp}^* = \text{-C}_5\text{Me}_5$

AU Le Bras, Jean; El Amouri, Hani; Besace, Yvon; Vaissermann, Jacqueline; Jaouen, Gerard

CS Ecole nationale superieure chimie Paris, Paris, 75231, Fr.

SO Bulletin de la Societe Chimique de France (1995), 132(10), 1073-82

CODEN: BSCFAS; ISSN: 0037-8968

PB Elsevier

DT Journal

LA English

AB Treatment of  $[\text{Cp}^*\text{Rh}(\text{CH}_3\text{CN})_3][\text{BF}_4]_2$  1a with PhOH at room temperature in dichloroethane afforded the asym. trimer  $[\{\text{Cp}^*\text{Rh}(\eta^6\text{-PhOH}\cdots)\}_2(\eta^5\text{-PhO}\cdots)\text{RhCp}^*][\text{BF}_4]_5$  2a in 87% yield, where the  $\eta$ -phenoxo species is hydrogen-bonded to the corresponding  $\eta$ -phenolic forms. The analogous iridium complex 2b was obtained from acetone/dichloroethane mixture in 80% yield. These species 2a and 2b were fluxional in solution, for instance, the variable temperature 1H NMR spectra for the rhodium species 2a show that the  $\eta\text{-Cp}^*$  signals coalesce at  $T = 354\text{ K}$  with  $\Delta G^\ddagger = 18 \pm 0.5\text{ kcal/mol}$ . A mechanism of exchange in accord with the exptl. data is proposed. Protonation of 2a by  $\text{HBF}_4\cdot\text{Et}_2\text{O}$  in acetone gave the unstable phenolic compound  $[\text{Cp}^*\text{Rh}(\eta^6\text{-PhOH})][\text{BF}_4]_2$  3a in 50% yield. On the other hand, 2a can be deprotonated by  $\text{NET}_3$  to give quant. the phenoxo derivative  $[\text{Cp}^*\text{Rh}(\eta^5\text{-PhO}\cdot\text{H}_2\text{O})][\text{BF}_4]$  4a. Compound 4a crystallizes in the orthorhombic space group  $\text{Ccm}21$ ,  $a = 17.469(3)\text{ Å}$ ,  $b = 28.845(4)\text{ Å}$ ,  $c = 14.115(2)\text{ Å}$ ,  $V = 7112(2)\text{ Å}^3$ ,  $Z = 16$ . The structure of 4a shows that the  $\text{-C:O}$  group of the Ph ring is bent upward with  $\theta = 14^\circ$ , and different from the structure of the ruthenium analog. The iridium species 2b behaved similarly when treated with  $\text{NET}_3$  to give an off-white compound  $[\text{Cp}^*\text{Ir}(\eta^5\text{-PhO}\cdot\text{H}_2\text{O})][\text{BF}_4]$  4b. When a yellow solution of  $[\text{Cp}^*\text{Rh}(\text{S})_3][\text{BF}_4]_2$  (S = coordinated solvent) was treated with  $17\beta\text{-estradiol}$  in acetone/THF, a mixture of four products  $(\alpha,\beta)\text{-}[\text{Cp}^*\text{Rh}(\eta^6\text{-estradiol})][\text{BF}_4]_2$  13ab and  $(\alpha,\beta)\text{-}[\text{Cp}^*\text{Rh}(\eta^5\text{-estradienonyl})][\text{BF}_4]$  14ab was obtained with  $\alpha/\beta$  ratio 9:1. In general the phenoxo form was more stable than the phenolic one for both  $\pi$ -bonded systems (phenol,  $17\beta\text{-estradiol}$ ). The effect of the counterion ( $\text{BF}_4$  and/or  $\text{CF}_3\text{SO}_3$ ) on the stability of the  $\pi$ -bonded phenolic forms (both systems) as well as the reactivity of the  $\pi$ -bonded phenoxo forms (both systems) towards electrophiles ( $\text{MeI}$ ,  $\text{CF}_3\text{SO}_3\text{Me}$ ) are compared and discussed.

L5 ANSWER 27 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

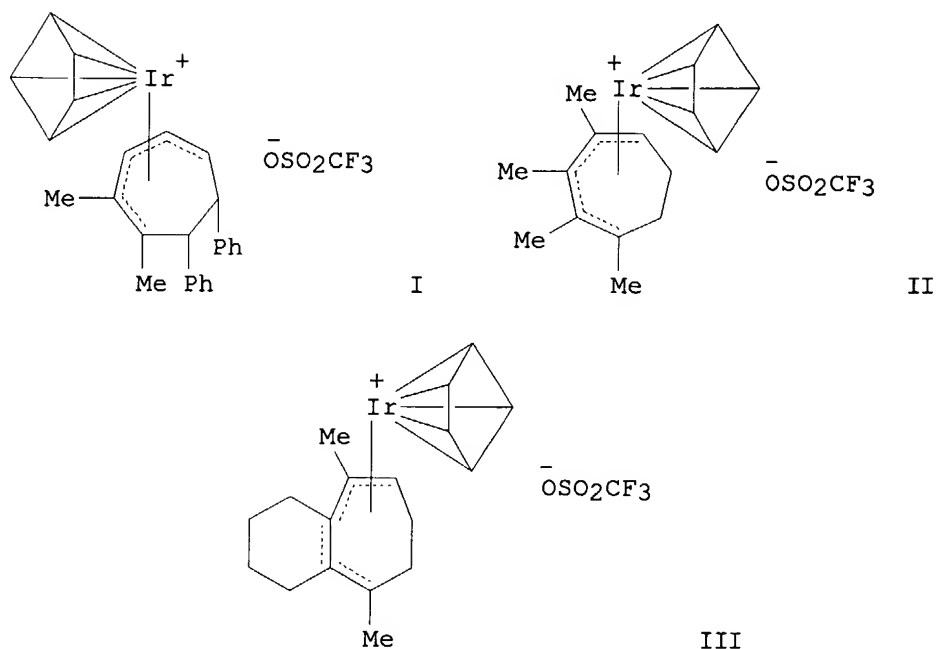
AN 1995:699349 CAPLUS

DN 123:228462

TI Transition Metal-Mediated [3 + 2 + 2] Allyl/Alkyne Cycloaddition Reactions. A New Reactivity Pattern for the Synthesis of Seven-Membered

# Carbocycles

AU Schwiebert, Kathryn E.; Stryker, Jeffrey M.  
 CS Department of Chemistry, University of Alberta, Edmonton, AB, T6G 2G2, Can.  
 SO Journal of the American Chemical Society (1995), 117(31), 8275-6  
 CODEN: JACSAT; ISSN: 0002-7863  
 PB American Chemical Society  
 DT Journal  
 LA English  
 OS CASREACT 123:228462  
 GI



AB The 1st examples of a metal-mediated [3 + 2 + 2] allyl/alkyne cycloaddn. reaction are reported, resulting in the transformation of a coordinated  $\eta^3$ -allyl ligand and two alkynes into a substituted  $\eta^5$ -cycloheptadienyl ring system. Formally homologous to Reppe-type alkyne cyclotrimerization, this unprecedented reactivity pattern provides a potentially exploitable three-component construction of seven-membered carbocycles. A single adduct 3 (shown as I) is isolated in modest yield from the reaction of  $[(\text{C}_5\text{Me}_5)\text{Ir}(\eta^3\text{-C}_3\text{H}_5)(\text{MeC}\equiv\text{CPh})_2]\text{OTf}$  2 with diphenylacetylene, but isomeric mixts. of two  $\eta^5$ -cycloheptadienyl complexes are formed on addition of either 1-phenylpropyne or phenylacetylene. Treatment of the neutral precursor  $(\text{C}_5\text{Me}_5)\text{Ir}(\eta^3\text{-C}_3\text{H}_5)\text{OTf}$  1 with excess 2-butyne or with 2,8-decadiyne also leads to  $\eta^5$ -cycloheptadienyl formation (9 and 11, shown as II and III, resp.), now in substantially higher yields. A mechanistic rationale is proposed, suggesting that this new reactivity pattern shares the same energy surface as that previously proposed for allyl alkyne cyclizations giving  $\eta^5$ -cyclopentadienyl and  $\eta^1, \eta^4$ -methanocyclohexadiene ring systems. In the present system, however, the regioselective migratory insertion that partitions the reaction between six- and seven-membered ring formation appears to be controlled by the nature of the ancillary ligand, with the sterically demanding, electron rich pentamethylcyclopentadienyl ligand promoting cycloheptadienyl formation

over competing pathways.

L5 ANSWER 28 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 1995:298344 CAPLUS  
DN 122:160890  
TI Surprisingly facile decomposition of the dication [cyclic]  
[(C5Me5)Ir(MeO-C6H4-CH2CO2NCOCH2CH2CO)]2+: a metal-mediated Hunsdiecker  
reaction of a succinimidyl ester?  
AU El Amouri, Hani; Gruselle, Michel; Vaissermann, Jacqueline; McGlinchey,  
Michael J.; Jaouen, Gerard  
CS Ecole Nationale Supérieure de Chimie de Paris, U.A. CNRS 403 11, rue  
Pierre et Marie Curie, Paris, 75231/05, Fr.  
SO Journal of Organometallic Chemistry (1995), 485(1-2), 79-84  
CODEN: JORCAI; ISSN: 0022-328X  
PB Elsevier  
DT Journal  
LA English  
OS CASREACT 122:160890  
GI

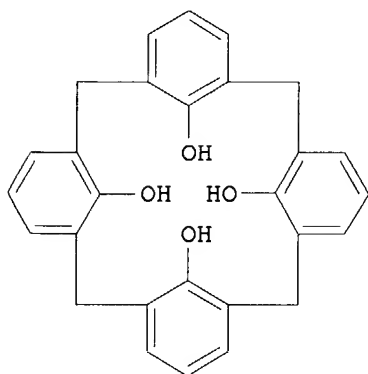
\* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT \*

AB A series of dicationic organoiridium complexes I (n = 1, 2, 3) were prepared  
in which the  $\pi$ -bonded Ph ring is attached to an alkyl chain terminated  
by a succinimidyl ester, thus forming Bolton-Hunter reagents for protein  
labeling. In solution, the benzyl derivative I (n = 1) underwent facile  
decomposition  
Loss of the succinimidyl moiety followed by decarboxylation led to  
dicationic complex II. This product was characterized spectroscopically  
and by x-ray crystallog. II crystallizes in the space group P21/a with a  
= 13.567(5) Å, b = 17.664(1) Å, c = 9.044(5) Å,  $\beta$  =  
90.15°, V = 2167 Å<sup>3</sup> and Z = 4. A rationale for this  
surprisingly facile decomposition invokes stabilization of the intermediate  
benzyl radical by the iridium.

L5 ANSWER 29 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 1995:142439 CAPLUS  
DN 122:133380  
TI  $\pi$ -Olefin iridium complexes. XXI. Synthesis and crystal structure of  
boat shaped synfacially  $\eta^3:\eta^3$ -benzene bridged heterobinuclear  
complexes  
AU Mueller, Joern; Escarpa Gaede, Petra; Qiao, Ke  
CS Institut fuer Anorganische und Analytische Chemie der Technischen  
Universitaet Berlin, Strasse des 17. Juni 135, Berlin, D-10623, Germany  
SO Journal of Organometallic Chemistry (1994), 480(1-2), 213-25  
CODEN: JORCAI; ISSN: 0022-328X  
PB Elsevier  
DT Journal  
LA German  
OS CASREACT 122:133380  
AB CpIr( $\eta^4$ -C6H6) (2) has been obtained in high yield by a four-step  
synthesis. Thermal reaction of 2 with [CpCo(C2H4)2] and photochem.  
reaction of 2 with [CpRh(C2H4)2] or [Cp\*Rh(C2H4)2] give the compds.  
 $\mu$ -( $\eta^3:\eta^3$ -C6H6)CoIrCp2 (3),  $\mu$ -( $\eta^3:\eta^3$ -C6H6)RhIrCp2  
(4), and  $\mu$ -( $\eta^3:\eta^3$ -C6H6)(RhCp\*)(IrCp) (5), resp. The x-ray  
crystallog. data of 3 and 4 reveal a boat-shaped conformation of the  
synfacially bridging benzene ligand with a rather long Co-Ir bond distance  
in 3 and a relatively short Rh-Ir bond length in 4 which are caused by  
almost constant folding angles of the benzene unit. The dynamic behavior of

the benzene bridge was investigated by NMR spectrometry.

L5 ANSWER 30 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 1995:132243 CAPLUS  
DN 122:56181  
TI Synthesis of cationic organometallic calixarene hosts by direct metalation  
of the outer face  
AU Steed, Jonathan W.; Juneja, Ravindra K.; Burkhalter, Robert S.; Atwood,  
Jerry L.  
CS Dept. Chem., Univ. Alabama, Tuscaloosa, AL, 35487, USA  
SO Journal of the Chemical Society, Chemical Communications (1994),  
(19), 2205-6  
CODEN: JCCCAT; ISSN: 0022-4936  
DT Journal  
LA English  
GI



I

AB Complexation of the aromatic rings of various calix[4]arenes, e.g., I, to transition metal containing moieties results in significant changes to the solubility, acidity and host-guest properties of the macrocycles.

L5 ANSWER 31 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 1993:638320 CAPLUS  
DN 119:238320  
TI Use of a Fourier deconvolution method in particle size determination and use of molecular mechanics in crystal structure determinations  
AU Su, Yingzhong  
CS Ames Lab., Ames, IA, USA  
SO Report (1992), IS-T-1591; Order No. DE92014510, 147 pp. Avail.: NTIS  
From: Energy Res. Abstr. 1992, 17(8), Abstr. No. 22008  
DT Report  
LA English  
AB A Fourier deconvolution method was employed to estimate the grain size from a recorded pattern. The usefulness of the method is very dependent on effects of noise and sampling discontinuities in the recorded patterns, and the treatment of data with a least squares spline smoothing method to ease their effects is discussed. The grain size results obtained by this program are compared with those obtained by Rietveld refinements and by transmission electron microscope investigations. X-ray structure detns. of single crystals of (I): benzo[2,3]-4-methylthiophene,  $C_9H_8S-Ir-[C_5(CH_3)_5]$ , and II: dibenzothiophene,  $C_{12}H_8S-Ir-[C_5(CH_3)_5]$  were performed. It had been expected that in the 2 compds. the Ir d-orbitals would be associated with the whole p-system of the complexing benzo-group, implying that all C atoms in this group would remain aromatic The x-ray

structure detns. and NMR 1H results indicate that both I and II can be best described as complexes in which 2 C atoms of a benzo-group of the ligand have been converted from sp<sup>2</sup> to sp<sup>3</sup> character. The structural results of the x-ray detns. and those of mol. mechanics are also compared and discussed. An optical alignment procedure making use of ordinary optical telescopes was developed which provides an easy-to-use alignment operation for the first stage of diffractometer alignment.

L5 ANSWER 32 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1993:259466 CAPLUS

DN 118:259466

TI Low-temperature chemical vapor deposition or laser photodeposition of metals on substrates by using organometallic compounds

IN Hicks, Robert F.; Kaesz, Herbert D.; Xu, Dagiang

PA University of California, Berkeley, USA

SO U.S., 8 pp. Cont.-in-part of U.S. Ser. No. 260,799, abandoned.

CODEN: USXXAM

DT Patent

LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 5130172	A	19920714	US 1989-428245	19891026 <--
PRAI	US 1988-260799		19881021		

AB Metals are deposited on Si or W substrates at .apprx.20-  
 ≤190° by using organometallic compound LnMRm in presence of H.  
 L in the compound is H, ethylene, allyl, methylallyl, butadienyl,  
 pentadienyl, cyclopentadienyl, methylcyclopentadienyl, cyclohexadienyl,  
 hexadienyl, cycloheptatrienyl, or a derivative of these compds. having  
 ≥1 C5 alkyl side chain; M is a metal that can readily cycle between  
 2 oxidation states and can catalyze hydrogenation of hydrocarbon ligands of  
 the compound; R is Me, Et, Pr, or Bu; and n and m are each a number from 0 to  
 the valence of the metal. The compound is vaporized at .apprx.20-  
 100°. M is selected from the group of metals having atomic number 22-29,  
 40-47, and 72-79 or 25-29, 42-47, and 74-79 or Co, Rh, Ir, Ni, Pd, Pt, Cu,  
 Ag, Au, and W.

L5 ANSWER 33 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1993:39130 CAPLUS

DN 118:39130

TI (η<sup>5</sup>-Pentamethylcyclopentadienyl)rhodium and -iridium compounds

AU White, C.; Yates, A.; Maitlis, P. M.; Heinekey, D. M.

CS Dep. Chem., Univ. Sheffield, Sheffield, S3 7HF, UK

SO Inorganic Syntheses (1992), 29, 228-34

CODEN: INSYA3; ISSN: 0073-8077

DT Journal

LA English

OS CASREACT 118:39130

AB Reaction of RhCl<sub>3</sub>·3H<sub>2</sub>O or IrCl<sub>3</sub>·xH<sub>2</sub>O with C<sub>5</sub>Me<sub>5</sub>H in MeOH  
 afforded the corresponding [M(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Cl<sub>2</sub>]<sub>2</sub> [M = Rh (95%), Ir (85%)].  
 Reaction of [Rh(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Cl<sub>2</sub>]<sub>2</sub> with AgPF<sub>6</sub> in MeCN gave  
 [Rh(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(NCMe)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> in 65% yield. Reaction of  
 [Ir(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Cl<sub>2</sub>]<sub>2</sub> with AgPF<sub>6</sub> in Me<sub>2</sub>CO gave [Ir(η<sup>5</sup>-  
 C<sub>5</sub>Me<sub>5</sub>)(OCMe<sub>2</sub>)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (91% yield) which was substituted with fluorene to  
 give [Ir(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(η<sup>6</sup>-C<sub>13</sub>H<sub>10</sub>)](PF<sub>6</sub>)<sub>2</sub>.

L5 ANSWER 34 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1992:470015 CAPLUS

DN 117:70015

TI Hydride addition to and reduction of Cp\*Ir(η<sup>6</sup>-BT)<sub>2</sub><sup>+</sup> and  
 Cp\*Ir(η<sup>6</sup>-DBT)<sub>2</sub><sup>+</sup>, where BT = benzo[b]thiophene and DBT =  
 dibenzothiophene

AU Chen, Jiabi; Su, Yingzhong; Jacobson, Robert A.; Angelici, Robert J.  
 CS Dep. Chem., Iowa State Univ., Ames, IA, 50011, USA  
 SO Journal of Organometallic Chemistry (1992), 428(3), 415-29  
 CODEN: JORCAI; ISSN: 0022-328X  
 DT Journal  
 LA English  
 OS CASREACT 117:70015  
 AB The benzo[b]thiophene (BT) complexes  $\text{Cp}^*\text{Ir}(\eta^6\text{-BTs})_2^+$  (BTs = BT (1a), 2-MeBT (1b), 3-MeBT (1c), 2,3-Me<sub>2</sub>BT (1d),  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) react with  $\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OMe})_2^-$  to add two H<sup>-</sup> to the coordinated arene ring of the BTs to give the cyclohexadiene complexes  $\text{Cp}^*\text{Ir}(\eta^4\text{-BTs}\cdot 2\text{H})$ , 2a-d. The dibenzothiophene complex  $\text{Cp}^*\text{Ir}(\eta^6\text{-DBT})_2^+$  (3) reacts similarly to give  $\text{Cp}^*\text{Ir}(\eta^4\text{-DBT}\cdot 2\text{H})$  (4). Both of these reactions can be reversed by adding  $\text{Ph}_3\text{C}^+$ . Two-electron redns. of 1c and 3 give the  $\eta^4$ -arene complexes  $\text{Cp}^*\text{Ir}(\eta^4\text{-3-MeBT})$  and  $\text{Cp}^*\text{Ir}(\eta^4\text{-DBT})$ . Compds. 2c and 4 were characterized by x-ray diffraction.

L5 ANSWER 35 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1992:235830 CAPLUS  
 DN 116:235830  
 TI Sequential displacement of coordinated ethene by hexafluorobenzene: crystal structures of  $\eta^2$ - and  $\eta^4$ -hexafluorobenzene complexes of iridium  
 AU Bell, Tanachat W.; Helliwell, Madeleine; Partridge, Martin G.; Perutz, Robin N.  
 CS Dep. Chem., Univ. York, York, YO1 5DD, UK  
 SO Organometallics (1992), 11(5), 1911-18  
 CODEN: ORGND7; ISSN: 0276-7333  
 DT Journal  
 LA English  
 AB The photochem. reaction of  $(\eta^5\text{-C}_5\text{R}_5)\text{Ir}(\text{C}_2\text{H}_4)_2$  (R = H, Me) with hexafluorobenzene effects sequential replacement of coordinated ethene by hexafluorobenzene, yielding  $(\eta^5\text{-C}_5\text{R}_5)\text{Ir}(\text{C}_2\text{H}_4)(\eta^2\text{-C}_6\text{F}_6)$  (I) followed by  $(\eta^5\text{-C}_5\text{R}_5)\text{Ir}(\eta^4\text{-C}_6\text{F}_6)$  (II). I is present in solution as two isomers which interconvert slowly compared with the NMR relaxation time, T<sub>1</sub>. The dominant isomer of I exhibits coupling between ethene nuclei and <sup>19</sup>F, suggestive of a C-H...F interaction. The minor isomer is postulated to be related to the major isomer by 180° rotation about the vector joining Ir to the midpoint of the coordinated C-C bond of C<sub>6</sub>F<sub>6</sub>. All the complexes exhibit three mutually coupled resonances in the <sup>19</sup>F NMR spectrum, indicating that the C<sub>6</sub>F<sub>6</sub> units are stereochem. rigid. The x-ray crystal structure of I and II (R = H) were determined

L5 ANSWER 36 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1992:41710 CAPLUS  
 DN 116:41710  
 TI Protonation of diene complexes of rhodium, iridium, ruthenium, and osmium: a fine balance between terminal and agostic hydrides  
 AU Bennett, Martin A.; McMahon, Ian J.; Pelling, Simon; Brookhart, Maurice; Lincoln, David M.  
 CS Res. Sch. Chem., Aust. Natl. Univ., Canberra, 2601, Australia  
 SO Organometallics (1992), 11(1), 127-38  
 CODEN: ORGND7; ISSN: 0276-7333  
 DT Journal  
 LA English  
 AB The structures of the cationic hydrido complexes formed on addition of HPF<sub>6</sub> to  $(\eta^5\text{-pentamethylcyclopentadienyl})$  and  $(\eta^6\text{-arene})\text{metal}$  complexes containing various 1,3-dienes or 1,5-cyclooctadiene (COD) have been investigated by IR and NMR (<sup>1</sup>H, <sup>13</sup>C) spectroscopy. The rhodium complexes  $[\text{RhH}(\eta^5\text{-C}_5\text{Me}_5)(\text{diene})]^+$  [diene = 1,3-cyclohexadiene (I), 2,3-dimethylbutadiene (II)] are highly fluxional  $\eta^3$ -enyl complexes

with a M-H-C interaction (agostic hydrides), as shown by their  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra at  $-100^\circ$  and by deuteration expts. As with other compds. of this class, two reversible processes can be observed by variable-temperature NMR spectroscopy: (1) M-H bond cleavage to give a  $\eta^3$ -enyl complex, which leads to exchange of the endo C-H bonds of I and exchange of the agostic Me hydrogen atoms of II; (2) C-H bond cleavage to give a diene metal hydride, which, in combination with process 1, av. sep. the endo and exo protons of I and the five dienyl protons of II. The free energy of activation  $\Delta G_{\text{thermod.}}$  for process 2 is slightly larger than for process 1, the estimated values being about 9.0 and 7.5 kcal/mol, resp., in the case of II. The complexes  $[\text{IrH}(\eta\text{-C}_5\text{Me}_5)(\text{diene})]^+$  [diene = 1,3-cyclohexadiene (III), 2,3-dimethylbutadiene (IV)] and  $[\text{OsH}(\eta\text{-arene})(\text{diene})]^+$  (arene =  $\text{C}_6\text{H}_6$ , diene = 1,3-cyclohexadiene, 2,3-dimethylbutadiene; arene = 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$ , diene = 1,3-cyclohexadiene, 2,3-dimethylbutadiene) are terminal hydrides in which the hydride ligand migrates between metal and diene reversibly and rapidly on the NMR time scale above room temperature ( $\Delta G_{\text{thermod.}}$  simeq. 12 kcal/mol for III and IV). The coupled  $^{13}\text{C}$  NMR spectrum of 1,3-cyclohexadiene complex  $[\text{RuH}(\eta\text{-C}_6\text{H}_6)(\text{C}_6\text{H}_8)]^+$  (V) at  $-100^\circ$  suggests that this compound contains an agostic hydride similar to I and II, but the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra above  $-100^\circ$  resemble those expected for a highly fluxional terminal hydrido diene complex, the free energy of activation  $\Delta G_{\text{thermod.}}$  for reversible Ru-H bond cleavage being 8.8 kcal/mol. In contrast to the Rh complexes and most other agostic hydrides formed from protonation of diene complexes, therefore,  $\Delta G_{\text{thermod.}}$  for C-H bond cleavage (process 2) in V is less than that for M-H bond cleavage (process 1) and is probably about 5-6 kcal/mol. The compds.  $[\text{RuH}(\eta\text{-C}_6\text{Me}_6)(\text{C}_6\text{H}_8)]^+$  and  $[\text{RuH}(\eta\text{-arene})(1,3\text{-diene})]^+$  (diene = 2,3-dimethylbutadiene, arene =  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_3\text{Me}_3$ ,  $\text{C}_6\text{Me}_6$ ; arene =  $\text{C}_6\text{Me}_6$ , diene = isoprene, 2-methyl-1,3-pentadiene, 3-methyl-1,3-pentadiene) are also agostic, but in most cases limiting spectra cannot be obtained, even for process 1, at  $-100^\circ$ . Protonation of  $\text{M}(\eta\text{-arene})(1,5\text{-COD})$  gives terminal hydrido diene complexes  $[\text{MH}(\eta\text{-arene})(1,5\text{-COD})]^+$  (M = Ru, arene =  $\text{C}_6\text{H}_6$ , 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$ ,  $\text{C}_6\text{Me}_6$ ; M = Os, arene =  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_3\text{Me}_3$ ). The compound obtained from  $\text{Ru}(\eta\text{-C}_6\text{Me}_6)(1,5\text{-COD})$  and  $\text{DPF}_6$  incorporates deuterium at the methylene carbon atoms of the coordinated diene, which implies that  $[\text{RuH}(\eta\text{-C}_6\text{Me}_6)(1,5\text{-COD})]^+$  is in equilibrium with  $\eta^1, \eta^2$ -cyclooctenyl and possibly agostic  $\eta^3$ -cyclooctenyl species. All the protonated diene complexes except  $[\text{OsH}(\eta\text{-arene})(1,5\text{-COD})]^+$  react with 2e-donor ligands (L) to give nonfluxional 18e complexes of the type  $[\text{M}(\eta\text{-C}_5\text{Me}_5)(\eta^3\text{-enyl})(\text{L})]^+$  (M = Rh, Ir, L = tert-BuNC) and  $[\text{M}'(\eta\text{-arene})(\eta^3\text{-enyl})(\text{L})]^+$  [M' = Ru, Os; L = CO, tert-BuNC,  $\text{P}(\text{OMe})_3$  (not all possible combinations)].

L5 ANSWER 37 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1992:6711 CAPLUS

DN 116:6711

TI  $\eta^1(\text{S})$ - and  $\eta^6$ -coordination of dibenzothiophene (DBT) in  $\text{Cp}^*\text{MCl}_2[\eta^1(\text{S})\text{-DBT}]$  and  $\text{Cp}^*\text{M}(\eta^6\text{-DBT})_2^+$  (M = iridium, rhodium;  $\text{Cp}^*$  = pentamethylcyclopentadienyl)

AU Rao, K. Mohan; Day, Catherine L.; Jacobson, Robert A.; Angelici, Robert J.

CS Ames Lab., Iowa State Univ., Ames, IA, 50011, USA

SO Inorganic Chemistry (1991), 30(26), 5046-9

CODEN: INOCAJ; ISSN: 0020-1669

DT Journal

LA English

OS CASREACT 116:6711

AB The dimers  $[\text{Cp}^*\text{MCl}_2]_2$  (M = Ir, Rh;  $\text{Cp}^*$  =  $\eta^5\text{-C}_5\text{Me}_5$ ) react rapidly with dibenzothiophene (DBT) to give the sulfur-coordinated DBT complexes  $\text{Cp}^*\text{MCl}_2[\eta^1(\text{S})\text{-DBT}]$  (I). The structure of the Ir complex was determined by single crystal x-ray anal. Upon reaction with  $\text{AgBF}_4$  followed by DBT,  $[\text{Cp}^*\text{MCl}_2]_2$  give the  $\eta^6\text{-DBT}$  complexes  $\text{Cp}^*\text{M}(\eta^6\text{-DBT})_2^+$ , which upon

reaction with Cl<sup>-</sup> give I.

L5 ANSWER 38 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1990:7672 CAPLUS

DN 112:7672

TI Ruthenium, rhodium, and iridium complexes of thiophene and benzo[b]thiophenes: models for catalytic hydrodesulfurization

AU Hockett, S. C.

CS Ames Lab., Ames, IA, USA

SO Report (1987), IS-T-1322; Order No. DE88007614, 191 pp. Avail.: NTIS

From: Energy Res. Abstr. 1988, 13(13), Abstr. No. 29295

DT Report

LA English

AB Ru, Rh, and Ir complexes of  $\pi$ -bound thiophene (T) and benzo[b]thiophenes (BTs), which serve as models for the adsorption of thiophenes on hydrodesulfurization (HDS) catalysts, have been synthesized. X-ray structural characterization of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\eta^6\text{-BT})]\text{BF}_4$  ( $\text{C}_5\text{H}_5$  = cyclopentadienyl) is reported. These model complexes react with nucleophiles  $[\text{H}^-, \text{MeO}^-, (\text{MeO}_2\text{C})_2\text{CH}^-, \text{EtS}^-, \text{and phosphines}]$ . The BT compds. yield isolable transition metal cyclohexadienyl complexes derived from fused ring aromatic ligands; four isomers of each cyclohexadienyl complex are produced. This isomer of  $\text{CpRu}(\text{BT}\cdot\text{H})$  (Cp = cyclopentadienyl) has been characterized by an x-ray structure determination

The

T complexes react with phosphines to produce  $[\text{Cp}^*\text{Ir}(\eta^4\text{-T}\cdot\text{PR}_3)]_2^+$ . Double nucleophilic addition reactions ( $\text{H}^-$  and  $\text{MeO}^-$ ) of  $[\text{Cp}^*\text{Ir}(\text{BT})]_2^+$  and  $[\text{Cp}^*\text{Ir}(3\text{-MeBT})]_2^+$  are also discussed. Reaction of either  $\text{NaBEt}_3\text{H}$  or  $\text{Cp}_2\text{Co}$  with  $[\text{Cp}^*\text{Ir}(\text{T})]_2^+$  results in a 2e<sup>-</sup> reduction of the Ir complex. This product is identified as  $\text{Cp}^*\text{Ir}(\eta^4\text{-T})$ . Both  $[\text{CpRu}(\text{BT})]^+$  and  $[\text{CpRu}(3\text{-MeBT})]^+$  undergo base-catalyzed deuterium exchange of H(2) and H(7) in  $\text{DOH}/\text{CD}_3\text{OD}$  solns. which follows the rate law,  $\text{rate} = k[\text{Ru complex}][\text{OH}^-]$ . The mechanism is proposed to involve rate-determining proton abstraction from either  $[\text{CpRu}(\text{BT})]^+$ , or  $[\text{CpRu}(3\text{-MeBT})]^+$ , followed by addition  $\text{D}^+$  from the  $\text{CD}_3\text{OD}$  solvent to give the deuterated BT complex. Heterogeneous reactor studies of D exchange of BT over several HDS catalysts  $[\text{PbMo}/6.2/\text{S}_8, 1\% \text{ Pt}-10\% \text{ Re}(\gamma\text{-Al}_2\text{O}_3), \text{Co}/0.25/\text{MoS}$ , and  $5\% \text{ Re}(\gamma\text{-Al}_2\text{O}_3)]$  and  $\gamma\text{-Al}_2\text{O}_3$  indicate that BT is activated to exchange at the 2- and 3-positions over the catalysts.

L5 ANSWER 39 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1989:240583 CAPLUS

DN 110:240583

TI Structure of 3-( $\eta^5$ -tetramethylcyclopentadienyl)-1-( $\eta^6$ -2,4,6-trimethylphenyl)propaneiridium(2+) tetrafluoroborate(1-) methanol solvate

AU Lumme, Paavo O.; Turpeinen, Urho; Kaganovich, V. S.; Kudinov, A. R.; Rybinskaya, M. I.

CS Dep. Chem., Univ. Helsinki, Helsinki, SF-00100, Finland

SO Acta Crystallographica, Section C: Crystal Structure Communications (1989), C45(4), 559-61

CODEN: ACSCEE; ISSN: 0108-2701

DT Journal

LA English

AB The title compound is orthorhombic, space group  $\text{Pnma}$ , with  $a$  28.313(6),  $b$  9.137(3), and  $c$  9.789(4) Å;  $d_m = 1.79(1)$  and  $d_c = 1.782$  for  $Z = 4$ . The final  $R = 0.095$  for 902 reflections. Atomic coordinates are given. In the bridged sandwich structure the Ir is bonded to the cyclopentadienyl and benzene rings of the organic ligand. The  $\text{BF}_4^-$  anions and the  $\text{MeOH}$  solvent mols. are more or less disordered in the structure, but they could be located from the difference Fourier map. The Ir complex cations form discrete units in the structure. The crystal structure is thermally rather labile and is held together mainly through van der Waals forces.



L5 ANSWER 40 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1989:193074 CAPLUS  
 DN 110:193074  
 TI Dicationic arene complexes of ruthenium, rhodium, and iridium with  $\omega$ -functional substituents  
 AU Kaganovich, V. S.; Kudinov, A. R.; Rybinskaya, M. I.  
 CS Inst. Elementoorg. Soedin., Moscow, USSR  
 SO Metalloorganicheskaya Khimiya (1988), 1(2), 294-7  
 CODEN: MEKHEX; ISSN: 0235-0114  
 DT Journal  
 LA Russian  
 GI For diagram(s), see printed CA Issue.  
 AB Treating  $[(\eta\text{-C}_6\text{H}_6)\text{Ru}(\eta\text{-C}_{10}\text{H}_8)]_2 \cdot 2\text{BF}_4^-$  ( $\text{C}_{10}\text{H}_8$  = naphthalene),  $[(\text{C}_5\text{Me}_5)\text{Ir}(\eta\text{-C}_{10}\text{H}_8)]_2 \cdot 2\text{BF}_4^-$  ( $\text{C}_5\text{H}_5$  =  $\eta^5$ -cyclopentadienyl), or  $[(\text{C}_5\text{Me}_5)\text{Rh}(\eta\text{-C}_6\text{H}_6)]_2 \cdot 2\text{BF}_4^-$  with  $\text{Ph}(\text{CH}_2)_n\text{X}$  ( $n = 3$ ,  $\text{X} = \text{vinyl}$ ,  $\text{CO}_2\text{Et}$ ;  $n = 2$ ,  $\text{X} = \text{Br}$ ,  $\text{OH}$ ;  $n = 1$ ,  $\text{X} = \text{OH}$ ) in  $\text{MeNO}_2$  gave 52-72% title compds. I ( $n = 1-3$ ;  $\text{X} = \text{vinyl}$ ,  $\text{Br}$ ,  $\text{OH}$ ) and II ( $\text{M} = \text{Ir}$ ,  $\text{Rh}$ ;  $n = 1-3$ ;  $\text{X} = \text{vinyl}$ ,  $\text{CO}_2\text{Et}$ ,  $\text{Br}$ ,  $\text{OH}$ ).

L5 ANSWER 41 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1988:601977 CAPLUS  
 DN 109:201977  
 TI Crystal and molecular structure of  $[3-(\eta^5\text{-tetramethylcyclopentadienyl})-1-(\eta^6\text{-mesityl})\text{propane}]\text{iridium(II) bistetrafluoroborate mononitromethane}$   
 AU Lumme, Paavo O.; Turpeinen, Urho; Kaganovich, V. S.; Kudinov, R. R.; Rybinskaya, M. I.  
 CS Dep. Chem., Univ. Helsinki, Helsinki, SF-00100, Finland  
 SO Journal of Organometallic Chemistry (1988), 348(2), 255-60  
 CODEN: JORCAI; ISSN: 0022-328X  
 DT Journal  
 LA English  
 AB The title compound is orthorhombic, space group  $\text{Pbcn}$ , with  $a$  26.812(18),  $b$  14.275(11), and  $c$  13.942(5) Å;  $d_m = 1.756(10)$  and  $d_c = 1.763$  for  $Z = 8$ . Final  $R = 0.052$  ( $R_w = 0.057$ ). Atomic coordinates are given. The structure is a bridged sandwich complex, with an Ir atom bonded to the cyclopentadienyl and benzene rings of the organic ligand. The solvent mols.  $\text{MeNO}_2$  and the  $\text{BF}_4^-$  anions are somewhat disordered in the structure, but were located from the difference Fourier maps. The Ir complex cations form discrete units in the structure. The crystal is thermally rather labile, and is held together mainly by Van der Waals forces.

L5 ANSWER 42 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1988:510615 CAPLUS  
 DN 109:110615  
 TI Reactions with metal-coordinated olefins. Part VI. Transition metal NMR spectroscopy. Part X. Protonated diolefin complexes: model systems for carbon-hydrogen activation via metal complexation  
 AU Buchmann, Brigitte; Piantini, Umberto; Von Philipsborn, Wolfgang; Salzer, Albrecht  
 CS Anorg.-Chem. Inst., Univ. Zurich, Zurich, CH-8057, Switz.  
 SO Helvetica Chimica Acta (1987), 70(6), 1487-506  
 CODEN: HCACAV; ISSN: 0018-019X  
 DT Journal  
 LA English  
 OS CASREACT 109:110615  
 AB Protonation of  $[\text{M}(\text{C}_5\text{R}_5)(\text{diene})]$  ( $\text{R} = \text{H}$ ,  $\text{Me}$ ;  $\text{M} = \text{Co}$ ,  $\text{Rh}$ ,  $\text{Ir}$ ; diene = 2,3-dimethylbutadiene, 1,3-cyclohexadiene;  $\text{C}_5\text{H}_5$  =  $\eta^5$ -cyclopentadienyl) with  $\text{HBF}_4$  gave cationic species which show fluxional behavior on the NMR time scale at room temperature. Depending on  $\text{R}$  and  $\text{M}$ , three different ground states are observed for these cationic complexes in the NMR spectra at low

temps. While for M = Ir a classical metal-hydride structure M-H is observed, the Co and Rh complexes show ground states with agostic H-bridges  $M \cdots H \cdots C$ . The protonated species are characterized by  $^1H$ ,  $^{13}C$  and  $^{103}Rh$  NMR spectra. Total line-shape anal. of the  $^1H$  and  $^{13}C$  spectra in the 298-154 K range gave the free enthalpies of activation  $\Delta G^\ddagger$  for Me rotation and 1,4-H shift in the agostic structures. The Rh complexes show the lowest  $\Delta G^\ddagger$  values for the 1,4-H shift and the strength of the agostic bond appears to decrease in the order  $CoC_5H_5 > CoC_5Me_5 > RhC_5H_5 > RhC_5Me_5$ . Stable allyl-halide complexes are formed on reaction with HCl, while protonation with  $HBF_4$ , in the presence of CO, gives high yields of  $[M(CO)(allyl)(C_5R_5)][BF_4]$ .

L5 ANSWER 43 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1988:437969 CAPLUS  
 DN 109:37969  
 TI A study of the syntheses and properties of the cobalt triad of metal complexes of [2n]cyclophanes  
 AU Plitzko, Klaus Dieter; Boekelheide, Virgil  
 CS Dep. Chem., Univ. Oregon, Eugene, OR, 97403, USA  
 SO Organometallics (1988), 7(7), 1573-82  
 CODEN: ORGND7; ISSN: 0276-7333  
 DT Journal  
 LA English  
 OS CASREACT 109:37969  
 GI For diagram(s), see printed CA Issue.  
 AB Syntheses of cyclopentadienyl (Cp) and pentamethylcyclopentadienyl (CpMe5) cobalt complexes of arenes have been investigated for preparing cobalt complexes of [2n]cyclophanes. The most general and most efficient method was that of generating the solvated ions of  $(\eta^5-Cp)Co^{2+}$ ,  $(\eta^5-CpMe_5)Co^{2+}$ , and  $(\eta^5-CpMe_5)Co^+$ , by the reaction of  $[(\eta^5-Cp)CoI_2]_2$  or  $[(\eta^5-CpMe_5)CoCl_2]_2$  with  $AgBF_4$  or  $TlPF_6$  in solvent, and then allowing these solvated ions to react with individual [2n]cyclophanes. In this manner the mono(capped) complexes I [ $M = (\eta^5-Cp)Co^{2+}$ ,  $(\eta^5-CpMe_5)Co^{2+}$ , and  $(\eta^5-CpMe_5)Co^+$ ] were made with [22](1,4)cyclophane, 4,5,6,7,8,12,13,15,16-octamethyl-[22](1,4)cyclophane, 12,13,15,16-tetramethyl-[22](1,4)cyclophane, 5,8,12,15-tetramethyl-[22](1,4)cyclophane, anti-[22](1,3)cyclophane, [23](1,3,5)cyclophane, [24](1,2,4,5)cyclophane, and 4,5,7,8-tetramethyl-[22](1,4)cyclophane. In addition, the bis(capped) complex II [ $M = (\eta^5-CpMe_5)Co^{2+}$ ] was made with [22](1,4)cyclophane, 4,5,7,8-tetramethyl-[22](1,4)cyclophane, and 5,8,12,15-tetramethyl-[22](1,4)cyclophane. In a similar fashion, solvates were made and used to synthesize the mono(capped) complexes I [ $M = (\eta^5-CpMe_5)Rh^{2+}$  and  $(\eta^5-CpMe_5)Ir^{2+}$ ] containing [22](1,4)cyclophane, [24](1,2,4,5)cyclophane, and anti-[22](1,3)cyclophane. Also II [ $M = (\eta^5-CpMe_5)Ir^{2+}$ ] complex of [22](1,4)cyclophane was prepared

L5 ANSWER 44 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1988:437964 CAPLUS  
 DN 109:37964  
 TI Hydrodesulfurization model complexes: nucleophilic addition to  $\pi$ -coordinated benzo[b]thiophenes and thiophene  
 AU Hockett, Sara C.; Angelici, Robert J.  
 CS Dep. Chem., Iowa State Univ., Ames, IA, 50011, USA  
 SO Organometallics (1988), 7(7), 1491-500  
 CODEN: ORGND7; ISSN: 0276-7333  
 DT Journal  
 LA English  
 OS CASREACT 109:37964  
 GI For diagram(s), see printed CA Issue.  
 AB The  $\pi$ -bound thiophene (T) and benzo[b]thiophene (BT) complexes  $[CpRu(BT)]^+$  ( $Cp = \eta^5-C_5H_5$ ),  $[Cp^*Ir(BT)]^{2+}$  (I,  $Cp^* = \eta^5-C_5Me_5$ ), and  $[Cp^*Ir(T)]^{2+}$  (II), models for the adsorption of thiophenic compds. to

hydrodesulfurization catalyst surfaces, react with a variety of nucleophiles [H-, MeO-, (MeO<sub>2</sub>C)<sub>2</sub>CH-, EtS-, and phosphines]. The BT complexes yield the first isolable transition metal cyclohexadienyl complexes, e.g. III, derived from fused ring aromatic ligands; four isomers of each cyclohexadienyl complex are produced. The isomers result from addition at the four carbons on the benzene ring; for the nucleophiles studied, addition occurs preferentially at the C closest to the S atom. This isomer, as observed in III, derived from hydride addition to I, was characterized by an x-ray structure determination. II reacts with phosphines to produce addition products IV (PR<sub>3</sub> = PMe<sub>3</sub>, PPh<sub>2</sub>Me, PPh<sub>3</sub>). Double nucleophilic addition reactions (H- and MeO-) of I and the 3-methylbenzo[b]thiophene analog are also discussed. Reaction of either NaBEt<sub>3</sub>H or Cp<sub>2</sub>Co with II results in a 2e reduction of II to give a tetrahapto T complex.

L5 ANSWER 45 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1988:406707 CAPLUS

DN 109:6707

TI Bridged cationic arene complexes of Group VIII metals

AU Kaganovich, V. S.; Kudinov, A. R.; Rybinskaya, M. I.

CS Inst. Elementoorg. Soedin., Moscow, USSR

SO Koordinatsionnaya Khimiya (1987), 13(7), 922-9

CODEN: KOKHDC; ISSN: 0132-344X

DT Journal

LA Russian

GI For diagram(s), see printed CA Issue.

AB The title compds., e.g., I (M = Rh, Ir, Co; X = BF<sub>4</sub>, PF<sub>6</sub>) were prepared by intramol. ligand exchange of dichlorides II (M = Rh, Ir) or the corresponding dicarbonylcobalt complex. A bridged dimesitylpropane Ru complex analogous to I was also prepared and characterized by <sup>1</sup>H NMR.

L5 ANSWER 46 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1988:120906 CAPLUS

DN 108:120906

TI Analysis of a quasi-reversible two-electron cyclic voltammetric wave for an organometallic iridium(III)/iridium(I) couple at platinum and mercury electrodes

AU Bowyer, Walter J.; Geiger, William E.

CS Dep. Chem., Univ. Vermont, Burlington, VT, 05405, USA

SO Journal of Electroanalytical Chemistry and Interfacial Electrochemistry (1988), 239(1-2), 253-71

CODEN: JEIEBC; ISSN: 0022-0728

DT Journal

LA English

AB (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ir(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)<sub>2</sub>+/<sub>3</sub> displays Nernstian 2-electron voltammetry at a Hg electrode, but quasi-reversible charge transfer kinetics at solid electrodes. Cyclic voltammetry (CV) peak shapes and sepns. change drastically from 1 solvent to another at Pt, ΔE<sub>p</sub> values being as small as 170 mV in Me<sub>2</sub>CO and as large as 350 mV in MeCN (v = 0.03 V/s). These variations arise from changes in the relative E° values of the 1-electron Ir(III)/Ir(II) and Ir(II)/Ir(I) couples, and from changes in charge-transfer rates. The Ir(II)/Ir(I) couple has a significantly lower charge-transfer rate than the Ir(III)/Ir(II) couple at Pt electrodes. The sensitivity of the CV curves to the relative E° values allows the approx. determination of the individual E° values for each 1-electron process. In contrast, Nernstian conditions allow only the average of the 2 one-electron E° potentials to be determined. Solvents with higher solvating power are shown to facilitate the thermodyn. of the 2-electron transfer process by moving E<sub>2</sub>° pos. with respect to E<sub>1</sub>°. Possible reasons for the abnormally slow charge transfer rates at Pt electrodes are discussed.

L5 ANSWER 47 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1988:112689 CAPLUS  
 DN 108:112689  
 TI Synthesis of cationic metallocyclophanes with arene and cyclopentadienyl ligands.  
 AU Kaganovich, V. S.; Kudinov, A. R.; Rybinskaya, M. I.  
 CS A. N. Nesmeyanov Inst. Organo-Elem. Comp., Moscow, 117334, USSR  
 SO Journal of Organometallic Chemistry (1987), 323(1), 111-21  
 CODEN: JORCAI; ISSN: 0022-328X  
 DT Journal  
 LA English  
 OS CASREACT 108:112689  
 GI For diagram(s), see printed CA Issue.  
 AB Previously unknown bridged cationic complexes (metallocyclophanes), i.e., I and II (M = Co, Rh, Ir), with arene and cyclopentadienyl ligands have been obtained by ligand exchange in CF<sub>3</sub>CO<sub>2</sub>H. Thus, treating areneruthenium dichloride dimer III with CF<sub>3</sub>CO<sub>2</sub>H, followed by HBF<sub>4</sub>, gave I.

L5 ANSWER 48 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1987:176637 CAPLUS  
 DN 106:176637  
 TI Biphenyl and diphenylmethane as  $\pi$ -arene ligands in cationic pentamethylcyclopentadienylrhodium(II) and iridium(III) complexes  
 AU Valderrama, M.; Scotti, M.; Prati, E.  
 CS Fac. Quim., Pontificia Univ. Catol. Chile, Santiago, Chile  
 SO Boletin de la Sociedad Chilena de Quimica (1986), 31(2), 53-8  
 CODEN: BOCQAX; ISSN: 0366-1644  
 DT Journal  
 LA English  
 AB [M(C<sub>5</sub>Me<sub>5</sub>)( $\eta$ -arene)]A<sub>2</sub> (arene = Ph<sub>2</sub>CH<sub>2</sub>, Ph<sub>2</sub>; A = BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>; M = Rh, Ir; C<sub>5</sub>Me<sub>5</sub> =  $\eta$ -5-pentamethylcyclopentadienyl) were prepared by treating [M(C<sub>5</sub>Me<sub>5</sub>)Cl<sub>2</sub>]<sub>2</sub> with Ag salts in the presence of the corresponding polycyclic arene. The complexes were characterized by elemental anal., <sup>1</sup>H NMR and IR spectra. The reactivity of the coordinated arene ligand was studied by exchange with  $\alpha$ - and  $\Pi$ -donor ligands. Attempts to obtain bimetallic compds. with the polycyclic arenes acting as a bridging ligand are briefly discussed.

L5 ANSWER 49 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1985:523690 CAPLUS  
 DN 103:123690  
 TI Structural consequences of electron-transfer reactions. 11. Electrochemically induced changes in hapticity in mixed-sandwich compounds of iridium and rhodium  
 AU Bowyer, Walter J.; Geiger, William E.  
 CS Dep. Chem., Univ. Vermont, Burlington, VT, 05405, USA  
 SO Journal of the American Chemical Society (1985), 107(20), 5657-63  
 CODEN: JACSAT; ISSN: 0002-7863  
 DT Journal  
 LA English  
 OS CASREACT 103:123690  
 GI For diagram(s), see printed CA Issue.  
 AB The electrochem. redns. of two sandwich complexes, [( $\eta$ -5-C<sub>5</sub>Me<sub>5</sub>)M( $\eta$ -6-C<sub>6</sub>Me<sub>6</sub>)]<sup>2+</sup> (I; C<sub>5</sub>Me<sub>5</sub> = pentamethylcyclopentadienyl; M = Rh, Ir), are reported. The reduction of I (M = Rh) occurred by 2 reversible one-electron transfers having E° values separated by several hundred mV. I (M = Ir) was reduced in a single 2-electron step with cyclic voltammetric peak sepsns. very dependent on electrode material. The neutral species of both metals were isolated and identified as ( $\eta$ -5-C<sub>5</sub>Me<sub>5</sub>)M( $\eta$ -4-C<sub>6</sub>Me<sub>6</sub>) (II) by <sup>1</sup>H NMR. II (M = Rh, Ir) were also prepared by chemical reduction of I using ( $\eta$ -5-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Co or ( $\eta$ -5-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co, resp. II (M = Rh) reacted with O<sub>2</sub>

in C6D6 to give the xylylene complex III.

L5 ANSWER 50 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1985:24794 CAPLUS

DN 102:24794

TI The selective reduction of benzene to cyclohexene mediated by platinum metal complexes: x-ray crystal structure of (2-6- $\eta$ -1-nitromethylcyclohexadienyl)(1-5- $\eta$ -pentamethylcyclopentadienyl)iridium(III) tetrafluoroborate

AU Grundy, Stephen L.; Smith, Arnold J.; Adams, Harry; Maitlis, Peter M.

CS Dep. Chem., Univ. Sheffield, Sheffield, S3 7HF, UK

SO Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry (1972-1999) (1984), (8), 1747-54

CODEN: JCDBTBI; ISSN: 0300-9246

DT Journal

LA English

AB Reduction of [LM(C6H6)]<sup>2+</sup> (I; M = Rh, Ir, L = pentamethylcyclopentadienyl; M = Ru, L = C6Me6) with AgBF<sub>4</sub> gave the  $\eta$ 5-cyclohexadienyl complexes [LM(C6H7)]<sup>+</sup> which were further reduced to [LM(C6H8)] (II; C6H8 =  $\eta$ 4-cyclohexadiene). Treatment of II with acid gave cyclohexene with 100% selectivity whereas reaction with HBF<sub>4</sub> in C6H6 regenerated I. The overall reaction consists of addition of 2 H<sup>-</sup> followed by 2 H<sup>+</sup> to coordinated C6H6, and a cycle catalytic in Pt can be constructed. The efficiency for reduction of C6H6 to cyclohexene decreases in the order Ir > Ru > Rh. The reactions of other nucleophiles with the C6H6 ring in I (M = Ir, L = pentamethylcyclopentadienyl) are also discussed; reaction with MeNO<sub>2</sub> in the presence of base gave [LIr(C6H6CH<sub>2</sub>NO<sub>2</sub>)] [BF<sub>4</sub>] (L = pentamethylcyclopentadienyl), the structure of which was determined by x-ray crystallog.

L5 ANSWER 51 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1985:6777 CAPLUS

DN 102:6777

TI Double nucleophilic attack on  $\eta$ 6-arene(pentamethylcyclopentadienyl)iridium dications. Routes from substituted benzenes to substituted cyclohexenes by addition of two hydrides and two protons

AU Grundy, Stephen L.; Maitlis, Peter M.

CS Chem. Dep., Univ. Sheffield, Sheffield, S3 7HF, UK

SO Journal of Organometallic Chemistry (1984), 272(2), 265-82

CODEN: JORCAI; ISSN: 0022-328X

DT Journal

LA English

AB The complexes [(C5Me5)Ir( $\eta$ 6-L)] [BF<sub>4</sub>]<sub>2</sub> (I; C5Me5 = pentamethylcyclopentadienyl; L = PhR, D3CC6D5, o-, p-xylene, tetralin; R = Me, CMe<sub>3</sub>, OMe, Cl, OH) were prepared from (C5Me5Ir)<sub>2</sub>Cl<sub>4</sub> (II) and L and reduced with NaBH<sub>4</sub> to the  $\eta$ 5-cyclohexadienyl complexes. Attack was exo at the arene and, except for PhOMe, never at the substituent. PhMe showed no site preference but PhCMe<sub>3</sub> was attacked preferentially para, and ortho. PhOMe was attacked ipso as well as ortho, meta (predominant), and para, and PhOH gave only the meta isomer. p-Xylene gave one isomer and o-xylene and tetralin gave two. Further reduction of I (R = CMe<sub>3</sub>, Me, Cl, OMe) with [(MeOCH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>AlH<sub>2</sub>]Na gave a mixts. of 1- and 2-substituted cyclohexa-1,3-diene complexes [CMe<sub>3</sub>, 2- (>95%); Me, 1- (25%), 2- (75%); Cl, 1- (>95%); OMe, 1- (33%), 2- (67%)]. I (L = p-xylene) gave a mixture of the  $\eta$ 4-1,4-dimethylcyclohexa-1,3- and 1,4-diene complexes. Treating the cyclohexadiene complexes with HCl gave the free substituted cyclohexenes and II. The product from PhCMe<sub>3</sub> was 92% 3-substituted cyclohexene; that isomer (65%) and the 1-isomer (34%) were formed from PhMe and the 1- (34%) and the 4-isomer (58%) were formed from ClPh. PhOH gave only cyclohexanone. Overall these reactions yield the cyclohexene from the substituted benzene by addition of two hydrides and two protons and the iridium was recycled.

L5 ANSWER 52 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1984:138650 CAPLUS

DN 100:138650

TI Cyclohexene rings

IN Grundy, Stephen Leonard; Maitlis, Peter Michael

PA Imperial Chemical Industries PLC, UK

SO Brit. UK Pat. Appl., 6 pp.

CODEN: BAXXDU

DT Patent

LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	GB 2114149	A1	19830817	GB 1982-36864	19821230 <--
PRAI	GB 1982-179	A	19820105		

AB Treating a dicationic Group VIII organometallic complex with 2 nucleophiles and 2 electrophiles gave compds. containing a cyclohexene ring. Thus,  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$  (I) reacted with  $\text{C}_6\text{H}_6$  and  $\text{AgBF}_4$  to give  $[(\text{C}_6\text{Me}_6)\text{Ru}(\text{C}_6\text{H}_6)](\text{BF}_4)_2$ , which was reduced with  $\text{NaBH}_4$  to give 86%  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-C}_6\text{H}_7)]\text{BF}_4$ . The latter was reduced using  $\text{Na}[\text{Al}(\text{OCH}_2\text{CH}_2\text{OMe})_2\text{H}_2]$  to give 70%  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^4\text{-C}_6\text{H}_8)]$ , which was treated with  $\text{HCl}$  to give 98% cyclohexene and 90% I.

L5 ANSWER 53 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1984:6788 CAPLUS

DN 100:6788

TI A new preparative route to cationic arene complexes of ruthenium(II), rhodium(III) and iridium(III).

AU Rybinskaya, M. I.; Kudinov, A. R.; Kaganovich, V. S.

CS A.N. Nesmeyanov Inst. Org.-Elem. Compd., Moscow, 117334, USSR

SO Journal of Organometallic Chemistry (1983), 246(3), 279-85

CODEN: JORCAI; ISSN: 0022-328X

DT Journal

LA English

AB The cationic arene complexes  $[\text{RuLL}_1]\text{X}_2$  [ $\text{L} = \text{C}_6\text{H}_6$ , 1,3,5-Me<sub>3</sub>C<sub>6</sub>H<sub>3</sub>;  $\text{L}_1 = \text{L}$ , MePh, H<sub>2</sub>NPh, EtOPh, p-Me<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>Me<sub>6</sub>, 1,3,5-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CO<sub>2</sub>H;  $\text{X} = \text{PF}_6$ , BF<sub>4</sub>] and  $[\text{M}(\text{C}_5\text{Me}_5)\text{L}_2]\text{X}_2$  ( $\text{C}_5\text{Me}_5$  = pentamethylcyclopentadienyl;  $\text{L}_2 = \text{L}$ , C<sub>6</sub>Me<sub>6</sub>;  $\text{M} = \text{Rh}$ , Ir) were prepared by direct exchange of Cl ligands in dimers  $[\text{RuLCl}_2]_2$  and  $[\text{M}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$  for  $\text{L}_1$  in F<sub>3</sub>CCO<sub>2</sub>H. The triply Cl-bridged complexes  $[\text{Ru}_2\text{L}_2\text{Cl}_3]\text{X}$  and  $[\text{M}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_3]\text{X}$  were obtained by reaction of these dimers with acids.

L5 ANSWER 54 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1982:455338 CAPLUS

DN 97:55338

TI The selective reduction of benzene to cyclohexane

AU Grundy, Stephen L.; Maitlis, Peter M.

CS Dep. Chem., Univ. Sheffield, Sheffield, S3 7HF, UK

SO Journal of the Chemical Society, Chemical Communications (1982), (7), 379-80

CODEN: JCCCAT; ISSN: 0022-4936

DT Journal

LA English

GI For diagram(s), see printed CA Issue.

AB Addition of H<sup>-</sup> to complexes I ( $\text{L} = \eta^6\text{-C}_6\text{Me}_6$ ,  $\text{M} = \text{Ru}$ ;  $\text{L} = \eta^5\text{-cyclopentadienyl}$ ,  $\text{M} = \text{Rh}$ , Ir) gave the corresponding cyclohexadiene complexes II in 56-83% yield. Treatment of II with  $\text{HCl}$  gave  $\geq 92\%$  cyclohexene together with dimers III, which were readily converted to  $\eta^6\text{-C}_6\text{H}_6$  complexes IV, the precursors of I. Alternatively, treatment of II with  $\text{BF}_3 \cdot 2\text{H}_2\text{O}$  in  $\text{C}_6\text{H}_6$  gave cyclohexene and directly regenerated IV.

L5 ANSWER 55 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1980:620919 CAPLUS  
 DN 93:220919  
 TI Pentamethylcyclopentadienylrhodium and -iridium complexes. Part 26.  
 Dicationic  $\eta^5$ -aniline and  $\eta^6$ -anisole complexes  
 AU Espinet, Pablo; Bailey, Pamela M.; Downey, Raymond F.; Maitlis, Peter M.  
 CS Dep. Chem., Univ. Sheffield, Sheffield, S3 7HF, UK  
 SO Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry  
 (1972-1999) (1980), (7), 1048-54  
 CODEN: JCDBTI; ISSN: 0300-9246  
 DT Journal  
 LA English  
 AB Dicationic complexes  $[M(C_5Me_5)L][PF_6]_2$  were prepared and characterized ( $M =$   
 Rh, Ir;  $C_5Me_5$  = pentamethylcyclopentadienyl;  $L = p\text{-}RC_6H_4NR_1R_2$ ;  $R, R_1, R_2 =$   
 H, H, H; H, H, Me; H, Me, Me; Me, H, H; Me, Me, Me; H, H, Ph). NMR and IR  
 spectra show that a 6-imino-1-5- $\eta$ -cyclohexadienyl form of  $L$  is a  
 significant contributor to the bonding in these complexes and accounts,  
 e.g., for the barrier to rotation about the C-N bonds observed in the  
 N-methylaniline and diphenylamine complexes. This was confirmed by  
 single-crystal x-ray structure anal. of  $[Rh(C_5Me_5)(PhNHMe)][PF_6]_2$ .  
 Related anisole complexes  $[M(C_5Me_5)(PhOMe)][PF_6]_2$  were also prepared; their  
 NMR spectra are not characteristic of an  $\eta^5$ -bonded benzene ring and  
 the anisole is, therefore, probably  $\eta^6$ -bonded. The Rh-anisole complex  
 is labile and the anisole is easily displaced by  $Me_2CO$ . Thus, in contrast  
 to Me, the OMe group does not significantly stabilize  $\eta^6$ -arene binding  
 in these complexes.

L5 ANSWER 56 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1980:604822 CAPLUS  
 DN 93:204822  
 TI Reactions of the  $\eta^6$ -benzene( $\eta^5$ -ethyltetramethylcyclopentadienyl)rh  
 odium(III) cation and related species with nucleophiles; the crystal  
 structure of  $[Rh(\eta^5\text{-}C_5Me_4Et)(\eta^5\text{-}C_6H_6P(O)(OMe)_2)][PF_6]$   
 AU Bailey, Neil A.; Blunt, Edward H.; Fairhurst, Geoffrey; White, Colin  
 CS Chem. Dep., Univ. Sheffield, Sheffield, S3 7HF, UK  
 SO Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry  
 (1972-1999) (1980), (5), 829-36  
 CODEN: JCDBTI; ISSN: 0300-9246  
 DT Journal  
 LA English  
 AB  $[Rh(\eta^5\text{-}C_5Me_4Et)(\eta^6\text{-}C_6H_6)][PF_6]_2$  (I;  $C_5Me_4Et =$   
 ethyltetramethylcyclopentadienyl) reacted with  $Li[AlH(OCMe_3)_3]$ ,  $TlL$  [ $HL =$   
 $(MeCO)_2CH_2$ ], and  $P(OR)_3$  ( $R = Me, Et$ ) to give  $[Rh(C_5Me_4Et)(\eta^5\text{-}$   
 $C_6H_6R_1)][PF_6]_2$  [II;  $R_1 = H, CH(OMe)_2, PO(OR)_2$ , resp.]. Displacement of  
 the coordinated  $C_6H_6$  ligand was a competing reaction, e.g. I with pyridine  
 gave  $[Rh(C_5Me_4Et)(py)_3][PF_6]_2$ . The crystal and mol. structure of II [ $R_1 =$   
 $PO(OMe)_2$ ] was determined from x-ray diffractometer data by the heavy atom  
 method and refined by least squares to  $R$  0.0697 for 903 observed reflections.  
 The cyclohexadienyl ring carried the phosphoryl group in an exo  
 conformation.  $[Rh(C_5Me_4Et)(C_6H_6)][BF_4]_2$  reacted reversibly with  $PBu_3$ ,  
 $PMe_2Ph$ , and  $NEt_3$  to give  $[Rh(C_5Me_4Et)(\eta^5\text{-}C_6H_6R)][BF_4]_2$  ( $R = Bu_3P$ ,  
 $PhPMe_2, Et_3N$ ).  $[M(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_6)]X_2$  ( $M = Co, X = BF_4$ ;  $M = Ir$ ,  
 $X = PF_6$ ) reacted with  $PBu_3$  or  $OMe^-$  to give  $[M(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}$   
 $C_6H_6R_3)]X_2$  ( $R = Bu_3P, OMe$ ). IR and  $^1H$ ,  $^{13}C$ , and  $^{31}P$  NMR spectra of the  
 complexes were determined

L5 ANSWER 57 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1978:7027 CAPLUS  
 DN 88:7027  
 TI Pentamethylcyclopentadienyl-rhodium and -iridium complexes. Part XII.  
 Tris(solvent) complexes and complexes of  $\eta^6$ -benzene, -naphthalene,  
 -phenanthrene, -indene, -indole, and -fluorene and  $\eta^5$ -indenyl and

-indolyl

AU White, Colin; Thompson, Stephen J.; Maitlis, Peter M.  
 CS Dep. Chem., Univ. Sheffield, Sheffield, UK  
 SO Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry (1972-1999) (1977), (17), 1654-61  
 CODEN: JCOTBI; ISSN: 0300-9246

DT Journal  
 LA English

AB [ML(L1)3][PF6]2 (I; M = Rh, Ir; L =  $\eta$ -pentamethylcyclopentadienyl; L1 = MeCN, Me2SO, pyridine) were isolated and the less stable complexes I (M = Rh, Ir; L1 = Me2CO, MeOH, CH2Cl2) were characterized in solution. The  $\eta^6$ -arene complexes [ML(L2)][PF6]2 (M = Rh, L2 = benzene, PhMe, m-xylene, mesitylene, fluorene, indole; M = Ir, L2 = PhMe, m-xylene, naphthalene, phenanthrene, indene, indole, fluorene) were prepared from solns. of I (M = Rh, Ir; L1 = Me2CO). Both the naphthalene and phenanthrene complexes are labile, but not fluxional; phenanthrene is bonded by the terminal 6-membered ring. Reaction of I (M = Rh, Ir; L1 = Me2CO) with indene gave the  $\eta^5$ -indenyl complex, which was reversibly protonated, with rearrangement, to the  $\eta^6$ -indene complex. The Ir (but not the Rh) indole complex also underwent reversible deprotonation to the  $\eta^5$ -indole complex. Protonation/deprotonation is fast and the rate-determining step in the overall reaction is the movement of the metal from the 5- to the 6-membered ring and vice versa. The Rh  $\eta^6$ -fluorene complex is very labile, but the Ir analog is deprotonated by base to give a fluorenyl complex of undetd. structure. An order of stability is given for  $\eta^5$ - and  $\eta^6$ -arenes bonded to Rh(III) and Ir(III) based on the ease of substitution of bonded arenes by free arenes.

L5 ANSWER 58 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1977:406172 CAPLUS  
 DN 87:6172  
 TI Pentamethylcyclopentadienylrhodium and -iridium complexes. Part XIII.  $\eta^5$ -Oxocyclohexadienyl and  $\eta^6$ -phenol complexes

AU White, Colin; Thompson, Stephen J.; Maitlis, Peter M.  
 CS Dep. Inorg. Chem., Univ. Sheffield, Sheffield, UK  
 SO Journal of Organometallic Chemistry (1977), 127(3), 415-21  
 CODEN: JORCAI; ISSN: 0022-328X

DT Journal  
 LA English

GI For diagram(s), see printed CA Issue.

AB The Me2CO solvent complexes [M( $\eta^5$ -C5Me5)(Me2CO)3][PF6]2, (M = Rh, Ir), prepared from [M( $\eta^5$ -C5Me5)Cl2]2 and AgPF6 in Me2CO, reacted with PhOH to give the H-bonded dimeric phenol complexes I; these were easily deprotonated with base to the corresponding  $\eta^5$ -oxocyclohexadienyl complexes II. An unstable  $\eta^6$ -phenol complex, [Ir(C5Me5)(PhOH)][PF6]2, was obtained on protonation of (I; M = Ir).

L5 ANSWER 59 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1977:5595 CAPLUS  
 DN 86:5595  
 TI  $\eta^6$ -Indene- and  $\eta^5$ -indole-(pentamethylcyclopentadienyl)-rhodium(II) and -iridium(III) hexafluorophosphates and their reversible deprotonation and rearrangement reactions to  $\eta^5$ -indenyl- and  $\eta^5$ -indolyl-complexes

AU White, Colin; Thompson, Stephen J.; Maitlis, Peter M.  
 CS Dep. Chem., Univ. Sheffield, Sheffield, UK  
 SO Journal of the Chemical Society, Chemical Communications (1976), (11), 409-10  
 CODEN: JCCCAT; ISSN: 0022-4936

DT Journal  
 LA English

GI For diagram(s), see printed CA Issue.



AB [M(C5Me5)(Me2CO)3](PF6)2 (M = Rh, Ir; C5Me5 = pentamethylcyclopentadienyl), prepared in situ by reaction of [M(C5Me5)Cl2]2 with AgPF6 in Me2CO, undergoes substitution reactions with indene and indole to give the corresponding complexes I (X = CH, N resp.), in which the metal is complexed to the 6-membered ring. Deprotonation of I (M = Rh, X = CH, N; M = Ir, X = N) and subsequent rearrangement gave the corresponding complexes II, in which the metal is bound to the 5-membered ring. A study of the interconversion of II (M = Ir, X = CH) + H+ .dblharw. I shows that protonation-deprotonation is fast and the rate determining step is the movement of the metal from the 5- to the 6-membered ring and vice-versa.

L5 ANSWER 60 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1972:564830 CAPLUS

DN 77:164830

TI Reactivity of coordinated ligands. XIII. Electrophilic substitution reactions of 1,3-cyclohexadiene complexes of rhodium(I) and iridium(I)

AU Johnson, B. F. G.; Lewis, J.; Yarrow, D. J.

CS Univ. Chem. Lab., Univ. Camb., Cambridge, UK

SO Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry (1972-1999) (1972), (19), 2084-9

CODEN: JCDTBI; ISSN: 0300-9246

DT Journal

LA English

AB Protonation and deuteration studies were performed on (1,3-cyclohexadiene)( $\pi$ -cyclopentadienyl)rhodium and -iridium complexes. In acid media, proton exchange occurred at the endo-methylene positions of the cyclohexadiene ligand via interaction with the metal. Reaction with Ph3CBF4 gave coordinated cyclo-hexadienium cations which were susceptible to nucleophilic attack to give exo derivs. Acetylation of the Rh complex gave the product of acetyl substitution of the  $\pi$ -cyclopentadienyl ring. Acid solns. of this complex exhibited H exchange both with endo-H of the coordinated cyclohexadiene and with H atoms at the 2, 3, 4, and 5 positions of the substituted  $\pi$ -cyclopentadienyl ligand.

L5 ANSWER 61 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1972:14695 CAPLUS

DN 76:14695

TI Pentamethylcyclopentadienylrhodium and -iridium complexes. VI.  $\pi$ -Arene,  $\pi$ -cyclohexadienyl, and  $\pi$ -pyrrolyl complexes

AU White, C.; Maitlis, P. M.

CS Dep. Chem., McMaster Univ., Hamilton, ON, Can.

SO Journal of the Chemical Society [Section] A: Inorganic, Physical, Theoretical (1971), (21), 3322-6

CODEN: JCSIAP; ISSN: 0022-4944

DT Journal

LA English

AB A new method for the preparation of  $\pi$ -arene and  $\pi$ -pyrrolyl complexes is described. The trifluoroacetates [M(C5Me5)(OCOCF3)2, H2O] (M = Rh, Ir) in F3CCO2H react with a variety of methylated benzenes to give [M(C5Me5)(arene)]2+. The  $\pi$ -arene complexes of Ir(III) are more stable than those of Rh(III) and their stability increases with increasing methylation. The complex [Rh(C5Me5)(p-xylene)]2+ undergoes rapid displacement of p-xylene by Me2SO to give [Rh(C5Me5)(Me2SO)3]2+. The  $\pi$ -arene complexes react with nucleophiles (NaBH4, MeLi) to give  $\pi$ -cyclohexadienyl complexes where the attacking group becomes the exo-substituent. The  $\pi$ -pyrrolyl complexes [M(C5Me5)(C4H4N)]+ are obtained in high yield from the trifluoroacetates and do not react with nucleophiles under these conditions.

L5 ANSWER 62 OF 62 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1971:3720 CAPLUS  
DN 74:3720  
TI Pentamethylcyclopentadienyl-rhodium and -iridium halides. III. Reactions with cyclohexadienes  
AU Moseley, K.; Maitlis, Peter M.  
CS Chem. Dep., McMaster Univ., Hamilton, ON, Can.  
SO Journal of the Chemical Society [Section] A: Inorganic, Physical, Theoretical (1970), (17), 2884-8  
CODEN: JCSIAP; ISSN: 0022-4944  
DT Journal  
LA English  
AB Dimeric dichloropentamethylcyclopentadienylrhodium and -iridium complexes  $[M(C_5Me_5)Cl_2]_2$  ( $M = Ir, Rh$ ) react with both cyclohexa-1,3- and -1,4-diene to give the  $\pi$ -cyclohexa-1,3-diene-(pentamethylcyclopentadienyl)rhodium (I) and -iridium complexes. During this reaction, isomerization of the uncomplexed cyclohexa-1,4- to the -1,3-diene occurred. I was a catalyst for the disproportionation of cyclohexa-1,3-diene to cyclohexene and benzene. This reaction was assisted by the presence of EtOH and base. Mechanisms for the complex formation, isomerization, and disproportionation are suggested.

(FILE 'HOME' ENTERED AT 22:38:32 ON 10 DEC 2004)

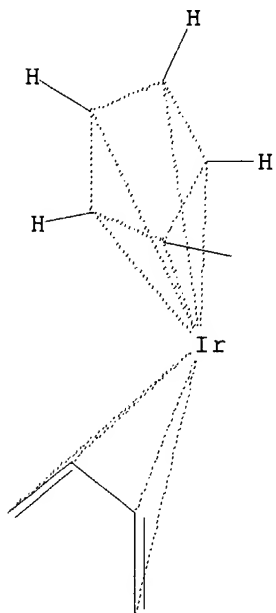
FILE 'REGISTRY' ENTERED AT 22:40:44 ON 10 DEC 2004

L1 STRUCTURE UPLOADED

=> d l1

L1 HAS NO ANSWERS

L1 STR



Structure attributes must be viewed using STN Express query preparation.

=> s l1

SAMPLE SEARCH INITIATED 22:42:35 FILE 'REGISTRY'

SAMPLE SCREEN SEARCH COMPLETED - 2768 TO ITERATE

36.1% PROCESSED 1000 ITERATIONS

0 ANSWERS

INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)

SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE \*\*COMPLETE\*\*

BATCH \*\*COMPLETE\*\*

PROJECTED ITERATIONS: 52205 TO 58515

PROJECTED ANSWERS: 0 TO 0

L2 0 SEA SSS SAM L1

=> s l1 full

FULL SEARCH INITIATED 22:42:40 FILE 'REGISTRY'

FULL SCREEN SEARCH COMPLETED - 55434 TO ITERATE

100.0% PROCESSED 55434 ITERATIONS

6 ANSWERS

SEARCH TIME: 00.00.01

L3 6 SEA SSS FUL L1

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FILE COVERS 1907 - 10 Dec 2004 VOL 141 ISS 25  
FILE LAST UPDATED: 9 Dec 2004 (20041209/ED)

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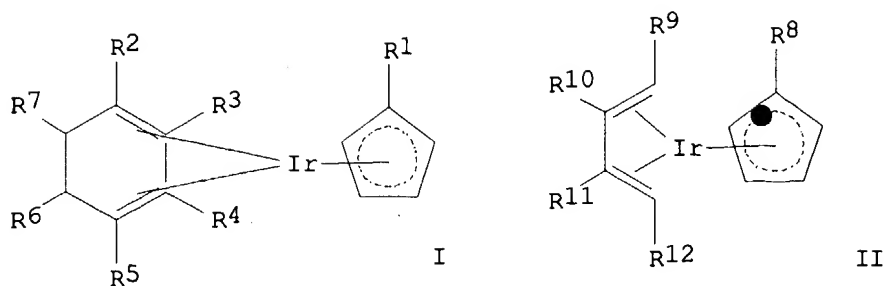
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L4                      7 L3

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L4    ANSWER 1 OF 7    CAPLUS    COPYRIGHT 2004 ACS on STN  
AN    2004:905686    CAPLUS  
DN    141:350278  
TI    Cyclohexadiene and butadiene iridium cyclopentadienyl compounds, their preparation, and use as CVD precursors for producing iridium-containing thin films  
IN    Takamori, Mayumi; Oshima, Noriaki; Kawano, Kazuhisa  
PA    Tosoh Corporation, Japan  
SO    U.S. Pat. Appl. Publ., 13 pp.  
      CODEN: USXXCO  
DT    Patent  
LA    English  
FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PI	US 2004215029	A1	20041028	US 2004-827448	20040420
PRAI	JP 2003-120109	A	20030424		
	JP 2003-120110	A	20030424		
	JP 2003-208975	A	20030827		
	JP 2003-420724	A	20031218		
	JP 2004-14454	A	20040122		
	JP 2004-63080	A	20040305		

GI



AB (cyclohexadiene)(cyclopentadienyl)iridium compds. I (R1 = H, lower alkyl; R2, R3, R4, R5, R6, R7 = H, halo, lower acyl, lower alkoxy, lower alkoxycarbonyl, lower alkyl, provided that the case where all of R1-R7 = H is excluded) and (butadiene)(cyclopentadienyl)iridium compds. II (R8 = lower alkyl; R9, R10, R11, R12 = H, halo, lower acyl, lower alkoxy, lower alkoxycarbonyl, lower alkyl, provided that the case where R8 = R9 = R11 = Me and R10 = R12 = H is excluded) are claimed; compds. I and II, having a low m.p., excellent vaporization characteristics and low film formation temperature on a substrate, are useful for forming an Ir-containing thin film by the

CVD process. I or II are prepared by reaction of an Ir compound with the corresponding cyclohexadiene or butadiene derivative and M+C5H4R1 or M+C5H4R8 (M = alkali metal, same R1, R8). Ir-containing thin films are produced by using the compound as a precursor by CVD process. In an example, CVD of precursor I (R1 = Et, R2-R7 = H, preparation given) onto a YSZ substrate at substrate temperature of 300° gave an Ir film; when the substrate temperature was 400°, an IrO2 film was obtained.

L4 ANSWER 2 OF 7 CAPLUS COPYRIGHT 2004 ACS on STN

AN 2004:898681 CAPLUS

DN 141:387034

TI Organometallic iridium compounds, processes for producing the same, and processes for producing thin films

IN Takamori, Mayumi; Oshima, Noriaki; Kawano, Kazuhisa

PA Tosoh Corporation, Japan

SO Eur. Pat. Appl., 23 pp.

CODEN: EPXXDW

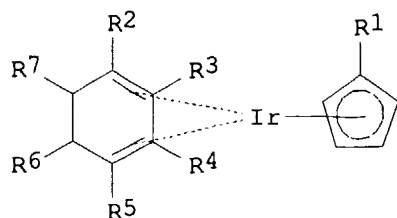
DT Patent

LA English

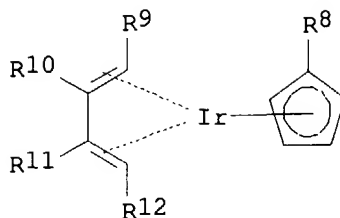
FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	EP 1471567	A1	20041027	EP 2004-8803	20040414
	R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, PL, SK, HR				
PRAI	JP 2003-120109	A	20030424		
	JP 2003-120110	A	20030424		
	JP 2003-208975	A	20030827		
	JP 2003-420724	A	20031218		
	JP 2004-14454	A	20040122		

GI



I



II

AB An organometallic compound having a low m.p., excellent vaporization characteristic and low film formation temperature on a substrate, for forming an Ir-containing thin film by the CVD process is provided. The organometallic Ir compound is represented by the following general formula I or II: in which R1 represents H or a lower alkyl group; R2 to R7 each represents H, a halogen, or the like, provided that specific combinations of R1 to R7 are excluded; R8 represents a lower alkyl group; R9 to R12 each represents H, a halogen, or the like, provided that specific combinations of R8 to R12 are excluded. Ir-containing thin films are produced by using the compound as a precursor by CVD process.

RE.CNT 16 THERE ARE 16 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 3 OF 7 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 2004:424179 CAPLUS  
DN 141:132197  
TI Ir thin films for PZT capacitors prepared by MOCVD using a new Ir precursor  
AU Fujisawa, H.; Watari, S.; Shimizu, M.; Niu, H.; Oshima, N.  
CS Department of Electrical Engineering and Computer Sciences, Graduate School of Engineering, Himeji Institute of Technology, Hyogo, 671-2201, Japan  
SO Materials Research Society Symposium Proceedings (2004), Volume Date 2003, 784(Ferroelectric Thin Films XII), 269-274  
CODEN: MRSPDH; ISSN: 0272-9172  
PB Materials Research Society  
DT Journal  
LA English  
AB Preparation of Ir thin films for PZT capacitors by MOCVD using a new liquid Ir precursor, Ir(EtCp)(CHD) was studied. Ir thin films with a highly reflecting surface and (111)-orientation were successfully obtained at 230-400°. When Ir(EtCp)(CHD) was used, shorter incubation time (20 min at 230° and not observed >240°) and higher nucleation d. (300-400 nm<sup>2</sup> at 250-300°) were observed because of its lower decomposition temperature (300°) than that of previously reported liquid precursor, Ir(EtCp)(COD). Resistivity of 100 nm-thick Ir films grown at 250-350° were <20 μΩ·cm. PZT capacitors with top and bottom electrodes prepared using Ir(EtCp)(CHD) showed D-E hysteresis loop with Pr of 15 μC/cm<sup>2</sup> and Ec of 60 kV/cm. No degradation of switching up to 1010 switching cycles by bipolar pulses of ±231 kV/cm (±3 V) and 500 kHz.

RE.CNT 15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 4 OF 7 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 2004:424160 CAPLUS  
DN 141:114299  
TI A novel iridium precursor for MOCVD  
AU Kawano, Kazuhisa; Takamori, Mayumi; Yamakawa, Tetsu; Watari, Soichi; Fujisawa, Hironori; Shimizu, Masaru; Niu, Hirohiko; Oshima, Noriaki

CS Tokyo Research Laboratory, TOSOH Corporation, Kanagawa, 252-1123, Japan  
 SO Materials Research Society Symposium Proceedings (2004), Volume Date 2003,  
 784(Ferroelectric Thin Films XII), 145-150  
 CODEN: MRSPDH; ISSN: 0272-9172  
 PB Materials Research Society  
 DT Journal  
 LA English  
 AB A novel liquid Ir precursor (1,3-cyclohexadiene)(ethylcyclopentadienyl)iridium, Ir(EtCp)(CHD), was synthesized and its phys. properties were examined. Ir(EtCp)(CHD) exhibited enough vapor pressure (0.1 torr/75°), excellent volatility and adequate decomposition temperature. Characteristics of the Ir films deposited using Ir(EtCp)(CHD) and the conventional Ir precursor (1,5-cyclooctadiene)(ethylcyclopentadienyl)iridium, Ir(EtCp)(COD), by metalorg. CVD (MOCVD) method were compared. Ir films grown using Ir(EtCp)(CHD) showed shorter incubation time and higher nucleation d. than those of films using Ir(EtCp)(COD).

RE.CNT 11 THERE ARE 11 CITED REFERENCES AVAILABLE FOR THIS RECORD  
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 5 OF 7 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 2004:292719 CAPLUS  
 DN 141:268758  
 TI A novel iridium precursor for MOCVD  
 AU Oshima, Noriaki; Kawano, Kazuhisa; Takamori, Mayumi; Yamakawa, Tetsu; Watari, Soichi; Fujisawa, Hironori; Shimizu, Masaru; Niu, Hirohiko  
 CS TOSOH Corporation Tokyo Research Center, Ayase, 252-1123, Japan  
 SO Proceedings - Electrochemical Society (2004), 2003-22(Physics and Technology of High-k Gate Dielectrics II), 231-235  
 CODEN: PESODO; ISSN: 0161-6374  
 PB Electrochemical Society  
 DT Journal  
 LA English  
 AB A novel iridium complex, (Cyclohexadiene)(ethylcyclopentadienyl)iridium, Ir(EtCp)(CHD), was synthesized and tested for metalorg. chemical vapor deposition (MOCVD) precursor. Iridium films were prepared on SiO<sub>2</sub>/Si substrate by MOCVD using new iridium precursor. (111)-Oriented Ir films were successfully grown on SiO<sub>2</sub>/Si. When Ir(EtCp)(CHD) was used as a precursor, higher nucleation d., smoother surface morphol. and shorter incubation time were observed than when conventional Ir precursor, Ir(EtCp)(COD), was used.

RE.CNT 9 THERE ARE 9 CITED REFERENCES AVAILABLE FOR THIS RECORD  
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 6 OF 7 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1986:130031 CAPLUS  
 DN 104:130031  
 TI A proton nuclear magnetic resonance, mass spectral and extended Hueckel study of some olefin complexes of rhodium(I) and iridium(I) and the crystal and molecular structure of  $\eta^4$ -2,4-dimethylpenta-1,4-diene( $\eta^5$ -formylcyclopentadienyl)rhodium(I)  
 AU Arthurs, Michael; Karodia, Haroon; Sedgwick, Mark; Morton-Blake, D. Antony; Cardin, Christine J.; Parge, Hans  
 CS Coll. Technol., Dublin Inst. Technol., Dublin, Ire.  
 SO Journal of Organometallic Chemistry (1985), 291(2), 231-51  
 CODEN: JORCAI; ISSN: 0022-328X  
 DT Journal  
 LA English  
 AB A 1H NMR study of monosubstituted  $\eta$ -cyclopentadienylrhodium(I) complexes of type LLRh(C<sub>5</sub>H<sub>4</sub>X) and -iridium(I) complexes of type L<sub>2</sub>Ir(C<sub>5</sub>H<sub>4</sub>X) (L = ethene, LL = 1,3- or 1,5-diolefin; X = CPh<sub>3</sub>, CHO, CO<sub>2</sub>Me) has been carried out. For complexes of both metals in which the neutral

ligand is ethene or a nonconjugated diolefin the NMR spectra of the cyclopentadienyl protons are unusual in that H(2), H(5) resonate to high field either at room temperature or below. The corresponding NMR spectra for the cyclopentadienyl ring protons of complexes where the neutral ligand is a conjugated diene are, with one exception, normal. A single crystal x-ray structural anal. of ( $\eta^4$ -2,4-dimethylpenta-1,4-diene)( $\eta^5$ -formylcyclopentadienyl)rhodium(I) (which exhibits an abnormal  $^1\text{H}$  NMR spectrum) reveals substantial localization of electron d. in the C(3)-C(4) cyclopentadienyl ring bond which may be consistent with a contribution from an allyl-ene rotamer to the ring-metal bonding scheme. An extended Hückel calcn. with self consistent charge iteration was performed on this complex. The results predict a greater Mulliken overlap population for the C(3)-C(4) bond in the cyclopentadienyl ring and show that the localization is dependent on both the cyclopentadienyl ring substituent and the nature of the diolefin. The mass spectral fragmentation patterns of some representative diene complexes of iridium(I) and rhodium(I) are presented.

L4 ANSWER 7 OF 7 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1971:3721 CAPLUS

DN 74:3721

TI Pentamethylcyclopentadienyl-rhodium and -iridium halides. II. Reactions with mono-, di-, and triolefins

AU Maitlis, Peter M.; Moseley, K.; Kang, Jung W.

CS Dep. Chem., McMaster Univ., Hamilton, ON, Can.

SO Journal of the Chemical Society [Section] A: Inorganic, Physical, Theoretical (1970), (17), 2875-83  
CODEN: JCSIAP; ISSN: 0022-4944

DT Journal

LA English

AB Dimeric dichloropentamethylcyclopenta-dienylrhodium and -iridium complexes,  $[\text{M}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$  ( $\text{M} = \text{Ir}, \text{Rh}$ ), reacted in ethanol in the presence of  $\text{Na}_2\text{CO}_3$  with butadiene, cycloheptatriene, and 6,6-diphenylfulvene, giving pentamethylcyclopentadienylrhodium(III) or -iridium(III) complexes of  $\pi$ -1-methylallyl,  $\pi$ -cyclohepta-2,4-dienyl, and (1,1-diphenylmethyl)cyclopentadienyl. Under similar conditions with  $[\text{Rh}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$ , norbornadiene and dicyclopentadiene gave pentamethylcyclopentadienylrhodium(I) diene complexes: ethylene gave bis(ethylene)rhodium(I) and -iridium(I) complexes. A hydrido-intermediate is implied in these reactions and both the hydrido- and deuteriochloro(triphenyl phosphine)pentamethylcyclopentadienyliridium complexes were isolated and characterized. With cyclopentadiene,  $[\text{Rh}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$  gave the cation and (cyclopentadienyl) - endo - H - pentamethylcyclopentadienylrhodium(I). (Cyclopentadienyl) - exo - H - pentamethylcyclopentadienylrhodium(I) was obtained by reduction of  $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{C}_5\text{H}_5)]^+$  with  $\text{NaBH}_4$  and was much more reactive than the endo-H-isomer. With halogenating agents  $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{C}_5\text{H}_5)]^+$  was the product, whereas the endo-H-isomer underwent cleavage to  $[\text{Rh}(\text{C}_5\text{Me}_5)\text{X}_2]_2$  and  $[\text{Rh}(\text{C}_5\text{H}_5)\text{X}_2]_2$ .  $[\text{Ir}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$  reacted with cyclopentadiene to give only the  $[\text{Ir}(\text{C}_5\text{Me}_5)(\text{C}_5\text{H}_5)]^+$  cation, which on reduction gave exo-H-Ir(C5Me5H)(C5H5) and Ir(C5Me5)(C5H6).